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Phosphorus losses from grasslands in short-term ley rotations under boreal conditions

Doctoral Dissertation

Mari Räty

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Abstract

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Grasslands occupy 45% of agricultural land in Finland, but in provinces characterised by grassland-based dairy production the proportion can be 67%. Phosphorus (P) loads from grasslands to inland waters have received relatively little research attention. In the Finnish climate, soils are subjected to frost in winter and snowfall comprises a considerable part of total annual precipitation. Surface runoff is generated by limited infiltration of snowmelt water into partially frozen soil in spring, which is a crucial period for dissolved nutrient and soil particle transport, especially in central and northern Finland.

This thesis examined the role of perennial grass vegetation in P dynamics in the soil-plant-water continuum and quantified P losses from grasslands under boreal conditions. Potential contributions of perennial vegetation to P losses were estimated indirectly, by determining changes in nutrient content of aboveground vegetation. Susceptibility of overwintering perennial ley regrowth to deliver P was assessed in a simulated snowmelt-induced surface runoff study. These approaches were complemented with five-year monitoring of a small (3.2 km^2) agricultural and forested catchment, representing grassland-based dairy production areas in east-central Finland. Amount and inter-annual variation in P losses and erosion rate were quantified.

The results showed that grasslands can release substantial amounts of plant-derived P when exposed to frost, freezing and thawing. Elevated P concentrations and losses of up to 0.69 kg ha^{-1} were detected in simulated snowmelt-induced runoff outflow. Higher P concentrations were also occasionally measured in early spring runoff at small catchment scale. More frequent freezing/thawing will enhance plant-derived P release, especially under a reduced snow layer and lack of insulating cover. In five-year monitoring of an agricultural sub-catchment with short-terms leys, where some fields were under grassland and others under cereals, mean annual total P (TP) losses were 1.0 kg ha^{-1} (range 0.6–1.5 kg ha^{-1}). The proportion of this TP load transported as dissolved reactive P (DRP) averaged 44% (range 32–56%) for the agricultural sub-catchment and 34% (28–38%) for the whole catchment area, reflecting low erosion rate under the protective grass cover. Five-year annual soil erosion rate from the agricultural sub-catchment was only 46–287 kg ha^{-1} (mean 115 kg ha^{-1} yr^{-1}). The results also suggested that P losses were partly associated with loss of organic material. These results indicate a need for P monitoring based on chemical analysis of water samples, instead of on turbidity measurements.

Grasslands are prone to DRP losses, but substantially less susceptible to erosion than arable fields during harvest years. In Finnish short-term ley rotations, grass leys are typically renovated every 3–4 years, often including autumn ploughing, which can increase erosion and particulate P losses. Thus when quantifying P loads to waters from short-term grass leys, erosion and nutrient losses within the whole ley cycle should be considered, including the ley establishment and renewal year.

Keywords: phosphorus, erosion, grassland, ley rotation, nutrient loading, surface runoff, winter

Tiivistelmä

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Suomessa nurmikasveja viljellään keskimäärin 45 prosentilla käytössä olevan maatalousmaan pinta-alasta (sisältää myös kesantoalan). Keskeisillä maidon- ja naudanlihantuotantoalueilla nurmi on pääasiallinen viljelykasvi. Perämeren rannikkoalueilla (Pohjanmaa, Keski- ja Pohjois-Pohjanmaa) nurmien osuus maatalousmaasta on keskimäärin 48 %, kun niiden keskimääräinen osuus voi olla jopa 67 % Vuoksen ja Kymijoen vesistöalueilla (Etelä- ja Pohjois-Savo, Pohjois-Karjala). Vaikka Pohjois-Savon pintavesien ekologinen tila on valtaosiltaan hyvä tai erinomainen, on etenkin Iisalmen reitillä hyvää huonommassa tilassa olevien vesien osuus merkittävä.

Tämän tutkimuksen yleisenä tavoitteena oli tuoda lisätietoa nurmiviljelyn aiheuttamasta vesistökuormituksesta boreaalisissa olosuhteissa. Tutkimuksessa selvitettiin lannoittamattomien suojakaistanurmien ja lannoitettujen säilörehunurmien maanpäälliseen kasvustoon talven ajaksi jääviä ravinnemääriä sekä arvioitiin kasvustoperäisen fosforin vapautumisalttiutta valumaveteen. Lisäksi selvitettiin, voidaanko säilörehunurmien niittoajankohdalla ja talveksi peltoon jäävän odelman määrällä vaikuttaa pintavalunnassa nurmelta huuhtoutuvaan fosforimäärään. Fosfori- ja kiintoainekuormituksen suuruutta ja vuosittaista vaihtelua tarkasteltiin pienen nurmiviljelyä edustavan peltovaltaisen osavaluma-alueen mittakaavassa (0,27 km^2, pelto-% 93). Tutkimusvaluma-alue (3,2 km^2) edusti kokonaisuudessaan tyypillistä pohjoissavolaista karjatalousaluetta (metsä-% 50, pelto-% 32, suo-% 18), jossa merkittävällä osalla pelloista viljellään nurmea.

Tulokset osoittivat, että monivuotisesta nurmikasvustosta voi potentiaalisesti vapautua valumaveteen huomattavia määriä fosforia, kun maanpäällinen biomassa altistuu kasvukauden jälkeen pakkaselle sekä toistuvalle jäätymiselle ja sulamiselle. Keväällä lumen sulamisen alkuvaiheessa myös valuma-alueen sulamisvesistä mitattiin ajoittain kohonneita liukoisen fosforin pitoisuuksia. Kun syksyllä nostetuilla nurmilaatoilla toteutettiin lumensulannan aiheuttama pintavalunnan simulointi, suurimmat kasvustomassat sisältäviltä nurmilaatoilta huuhtoutui fosforia jopa 0,69 kg ha^{-1}. Vähäluminen ja ilman pysyvää lumikerrosta oleva talvi altistaa kasvuston toistuvalle jäätymiselle ja sulamisella ja voi tehostaa kasvustoperäisen fosforin vapautumista valumaveteen.

Viiden vuoden seurantajaksolla kokonaisfosforia huuhtoutui peltovaltaiselta osavaluma-alueelta keskimäärin 1,0 kg ha^{-1} v^{-1} (vaihteluväli 0,6−1,5 kg ha^{-1} v^{-1}) ja koko tutkimusvaluma-alueelta 0,8 kg ha^{-1} v^{-1} (0,3−1,1 kg ha^{-1} v^{-1}). Liukoisen fosforihuuhtouman osuus kokonaisfosforihuuhtoumasta oli peltovaltaisella osavaluma-alueella keskimäärin 44 % (32−56 %) ja koko tutkimusvaluma-alueella 34 % (28−38 %). Kiintoainekuormitus oli keskimäärin vain 115 kg ha^{-1} v^{-1} (46−287 kg ha^{-1} v^{-1}) peltovaltaiselta osavaluma-alueelta ja 80 kg ha^{-1} v^{-1} (26−192 kg ha^{-1} v^{-1}) koko tutkimusvaluma-alueelta.

Tämä työ vahvisti, että nurmipeitteisestä maasta eroosio on vähäistä, mutta leville suoraan käyttökelpoisena pidetty liukoinen fosfori muodostaa huomattavan osan valumaveden kokonaisfosforista. Tulokset myös osoittivat, että nurmivaltaisilta alueilta peräisin oleva fosforihuuhtouma kytkeytyy osin orgaanisen aineksen huuhtoumaan. Peltovaltaisen osavaluma-alueen vesinäytteiden kiintoaineksen ja kokonaisfosforin pitoisuuksien välistä riippuvuussuhdetta kuvaava selitysaste jäi heikoiksi. Nurmi- ja metsävaltaisilla ja karkeampia maalajeja edustavilla valuma-alueilla, joissa liukoinen fosfori muodostaa merkittävän osan kokonaisfosforihuuhtoumasta, on laboratoriossa analysoitavilla vesinäytteillä keskeinen merkitys fosforikuormituksen seurannassa. Koska muutokset viljely- ja muokkauskäytännöissä vaikuttavat nurmiviljelyn ravinne- ja kiintoaineshuuhtoumiin, tulisi niitä tarkastella koko nurmikierron osalta, joka sisältää myös uusimis- ja perustamisvaiheita.

Asiasanat: fosfori, eroosio, nurmet, nurmiviljely, pintavalunta, ravinnekuormitus, talven olosuhteet

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Maaninka, October 2020 Mari Räty

List of original publications

The thesis is based on the following three publications, which are referred to by their Roman numerals in the text:

I. Räty, M., Uusi-Kämppä, J., Yli-Halla, M., Rasa, K. & Pietola, L. 2010. Phosphorus and nitrogen cycles in the vegetation of differently managed buffer zones. Nutrient Cycling in Agroecosystems 86: 121–132. https://doi.org/10.1007/s10705-009-9277-4.

II. Saarnio, S., Räty, M., Hyrkäs, M. & Virkajärvi, P. 2018. Biochar addition changed the nutrient content and runoff water quality from the top layer of a grass field during simulated snowmelt. Agriculture, Ecosystems and Environment 265: 156−165. https://doi.org/10.1016/j.agee.2018.06.007.

III. Räty, M., Järvenranta, K., Saarijärvi, E., Koskiaho, J. & Virkajärvi, P. 2020. Losses of phosphorus, nitrogen, dissolved organic carbon and soil from a small agricultural and forested catchment in east-central Finland. Agriculture, Ecosystems and Environment 302: 107075. https://doi.org/10.1016/j.agee.2020.107075.

This thesis also contains previously unpublished data.

Author′s contribution to the articles

I. The experimental design was planned by Liisa Pietola, Markku Yli-Halla and Mari Räty. Mari Räty conducted the field and laboratory work, processed the results and prepared the manuscript. All co-authors commented on the manuscript.

II. The original idea for the research was developed by Sanna Saarnio. The experimental design was planned jointly by Sanna Saarnio, Mari Räty, Perttu Virkajärvi and Maarit Hyrkäs. Mari Räty had the main responsibility for implementation of the experiment and calculation of the results, Maarit Hyrkäs carried out the statistical analysis, and all co-authors took part in interpretation of the results. Sanna Saarnio prepared the manuscript, with Mari Räty and Maarit Hyrkäs, and Perttu Virkajärvi commented on the manuscript.

III. Perttu Virkajärvi, Kirsi Järvenranta and Erkki Saarijärvi planned and established the catchment-scale monitoring system in 2010. In the study period 2011–2015, Mari Räty had the main responsibility for the research and field work. Mari Räty calculated and processed the results and had the main responsibility for preparing the manuscript. Perttu Virkajärvi, Kirsi Järvenranta, Erkki Saarijärvi and Jari Koskiaho took part in interpreating of the results and preparation of the manuscript.

Abbreviations

AB-horizon	Soil horizon, A horizon transitional to B (identified at depth 16−38 cm)
Al	Aluminium
Bw-horizon	Soil horizon, altered by weathering (identified at depth 38−45 cm)
BZ	Buffer zone
C	Carbon
Ca	Calcium
CEC_{pot}	Potential cation exchange capacity
DIN	Dissolved inorganic nitrogen
DM	Dry matter
DON	Dissolved organic nitrogen
DOC	Dissolved organic carbon
DRP	Dissolved reactive phosphorus
EPC	Equilibrium phosphorus concentration
EU	European Union
Fe	Iron
Fe^{2+}	Ferrous iron
Fe^{3+}	Ferric iron
HO^-	Hydroyxl groups
H_2O-P	Water-extractable phosphorus
H_2SO_4	Sulphuric acid
K	Potassium
LSD	Least significant difference
LSU	Livestock unit
N	Nitrogen
$NaHCO_3$-P	Sodium bicarbonate-extractable phosphorus
NaOH	Sodium hydroxide
NH_4Cl	Ammonium chloride
NH_4F	Ammonium fluoride
NH_4-N	Ammonium-nitrogen
NO_3-N	Nitrate-nitrogen
OC	Organic carbon
OM	Organic matter
P	Phosphorus
P_{Ac}	Acid ammonium acetate-extractable phosphorus
PP	Particulate phosphorus
SD	Standard deviation
SED	Standard error of the difference
SEM	Standard error of the mean
TN	Total nitrogen
TP	Total phosphorus
TSS	Total suspended solids

Contents

1. Introduction

1.1. Background

Despite huge amounts of scientific research during past and present decades, phosphorus (P) is still a highly relevant topic due to its agronomic and environmental implications. Phosphorus is an essential element in all biological systems and therefore the world's agricultural production is heavily dependent on the use of P fertilisers. Phosphorus is the 11th most abundant element in the lithosphere (Stevenson and Cole 1999) and exists in over 150 different mineral forms (Pierzynski et al. 2005), but most rocks usually contain P in relatively low concentrations. In natural systems, P is derived through weathering and dissolution from rock minerals, with apatite (compound of tricalcium phosphate $3[Ca_3(PO_4)_2] \times CaX_2$), and chloro-, fluor-, hydroxyl- and carbonate-apatites being the most common minerals (Stevenson and Cole 1999). Carbonate apatite is the most important phosphate mineral in sedimentary and igneous phosphate rock deposits used as raw material for producing P fertilisers. To compensate for *e.g.* P adsorption on soil particles, crop plant P requirements are generally secured by applying more P than is removed in the harvested crop, leading to P accumulation in soils as legacy P (*e.g.* Hooda et al. 2000, Syers et al. 2008). Excessive accumulation of P in surface soil is considered to be a major problem with agricultural soils, increasing the risk of P losses to water bodies (Withers et al. 2000).

For agricultural soils in the European Union (EU) that receive P inputs in fertiliser and manure or from other sources, the average net P balance is estimated to be around 4.9 kg ha^{-1} yr^{-1} in 2005. In the EU Member States, the P balances ranged from 23 kg ha^{-1} yr^{-1} (Belgium) to -2.8 kg ha^{-1} yr^{-1} (Slovakia), depending on e.g. different management practices (including type and efficiency of crop and animal production) and weather conditions (van Dijk et al. 2016). With increasing knowledge of the build-up of soil P in arable areas and associated losses of agricultural P to surface waters, contributing to eutrophication, the research emphasis has turned from agronomic to environmental aspects in recent decades in *e.g.* the USA and Western Europe. Phosphorus transfer from agricultural soils to waters via runoff and leaching is one of the key components of the P cycle with implications for water quality. At global scale, accelerated soil erosion and subsequent P losses in runoff result primarily from overgrazing and changes in land use due to conversion of grassland and forest soils with lower erodibility into annual croplands with higher erodibility (Smil 2000). The mean annual rate of soil loss by sheet and rill erosion amounts to 2.7−3.6 t ha^{-1} for European arable lands, with a large temporal and spatial variation (Cerdan et al. 2010, Panagos et al. 2015). The highest mean annual erosion rate is found for bare land (15 t ha^{-1}) and the lowest for grassland, shrub land and forest (< 1 t ha^{-1})(Cerdan et al. 2010). Worldwide, average anthropogenic P losses in dissolved form range from less 0.1% to almost 5% of P applied as inorganic fertiliser, representing approximately 1 Mt P per annum (Smil 2000). Along with the recent re-eutrophication trend in *e.g.* Lake Erie (Watson et al. 2016), studies are also increasingly concentrating on dissolved P instead of suspended solids and associated particulate-bound P losses.

In Finland, the most heavily eutrophied lakes are found on the west coast and in the inland area in North Savo in east-central Finland (Pietiläinen and Räike 1999). The lake-rich North Savo lies within the Vuoksi River Basin District, which contains around 36% of lake areas in eight Finnish River Basin Management Areas within different ecological state categories (Tattari and Väisänen 2011). In North Savo, 22% of lakes and 33% of rivers are not of good ecological water status, especially in the eutrophic Iisalmi Route, in which lakes are typically shallow and contain high concentrations of dissolved humic substances. In this region, agriculture has been set further targets on reducing diffuse P loads to aquatic recipients (Vallinkoski et al. 2016). Agriculture in the region is characterised by grassland-based dairy production. At the European scale, 73% of overall diffuse losses of nitrogen (N) (6.0 Tg N yr^{-1}) and P (0.025 Tg P yr^{-1}), estimated as dissolved inorganic P losses from agriculture, are related to livestock production systems, in particular feed production (Leip et al. 2015). In Finland, around 70% of P and of N in harvested agricultural plants are directly utilised as feed in animal production, of which some P and N are recycled back to the soil, mainly as manure (Antikainen et al. 2005).

1.2. Diffuse phosphorus loads from agricultural land

In the period 1981−2010, total phosphorus (TP) loads from Finnish agricultural land to surface waters varied between 2400 and 2700 t yr^{-1} (Tattari et al. 2017). The average nutrient load was found to increase with increasing percentage of arable land, explaining 90% and 95% of the variation in TP and total nitrogen (TN) losses, respectively (Tattari et al. 2017). Based on long-term monitoring data from 34 small agricultural catchments, mean annual TP losses vary from 0.09 to 7.5 kg ha^{-1} in catchments in the Baltic and Nordic countries, showing large interannual variation within catchments (Pengerud et al. 2015). Variations in annual P losses are primarily controlled by weather-driven fluctuations in water discharge volume (Vuorenmaa et al. 2002, Puustinen et al. 2005, Pengerud et al. 2015), which may easily mask land use- or agricultural practice-induced changes in the magnitude of losses. Pengerud et al. (2015) associated the highest P losses with *e.g.* high precipitation producing high specific runoff, in combination with relatively high soil P status and erosion risk.

Phosphorus is transported from agricultural soils to recipient waters in dissolved and particulate P (PP) form, bound to eroded soil particles. Membrane filtration is used to separate dissolved and particulate P fractions, but P in the dissolved fraction is also associated with inorganic and organic colloidal-sized particles (1 nm−1 µm) (Turtola 1996, Hens 1999, Hens and Merckx 2002, Heathwaite et al. 2005). In this thesis dissolved P is referred to as dissolved reactive P (DRP), *i.e*. the amount obtained when water samples are filtered through a ≤0.45 µm membrane filter, but not digested. Dissolved reactive P is considered to be fully available to algae, while the average bioavailability of PP is around 5% (range 0−13%) in Finnish rivers receiving agricultural loads, as determined in algal assays (Ekholm 1994).

Phosphorus is most commonly the nutrient limiting biological productivity in freshwaters and it is thus widely recognised as contributing to accelerated eutrophication of receiving freshwaters. Eutrophication leads to deterioration of water quality, *e.g.* blooms of blue-green algae (*e.g.* Wetzel 1983, Kauppi 1984, Sharpley and Rekolainen 1997, Correll 1998). As a result of internal P loading, accumulated P is recycled from bottom sediments back to the overlying water column, driven by *e.g.* biological activity and re-suspension. Internal P loading often delays lake recovery following a reduction in external P loading (Koski-Vähälä and Hartikainen 2001, Søndergaard et al. 2001, Welch and Cooke 2005). In freshwater bodies, the P concentration associated with eutrophication is considered to be 10−30 µg l^{-1} for DRP and 35−100 µg l^{-1} for TP (Pierzynski et al. 2005). However, TP concentrations above 20 µg l^{-1} are often regarded as problematic in most surface waters (Correll 1998). In Finnish inland waters, P is also considered to be a primary limiting nutrient, especially in the largest lakes and waterways, whereas some smaller oligotrophic lakes may be P- and N-limited and N alone may limit algal growth in very humic and heavily eutrophied lakes (Pietiläinen and Räike 1999).

Agriculture is regarded as the main source of diffuse P loads to surface waters and marine areas in the Baltic-Nordic countries (*e.g.* Vagstad et al. 2001). In the whole of Finland, P and N removal efficiency from industrial and municipal wastewaters in 2014 was 93% and 38%, respectively (Räike et al. 2020). In the period 1975−2000, efficient P removal from point sources resulted in a decreasing trend in TP concentrations in previously heavily point source-loaded lakes and rivers. However, in smaller lakes and rivers polluted by diffuse loading, the trend was for a slight increase in TP in the same period (Räike et al. 2003). Based on national monitoring data, Ekholm et al. (2015) estimated the TP and TN loads transported by 21 Finnish rivers to the northern Baltic Sea in the period 1985−2006. They found that the flow-adjusted agricultural TP loads decreased from 1985 to 2006, especially in rivers discharging to the Bay of Bothnia in western Finland (by up to 30%), whereas the TN fluxes showed the opposite trend, increasing by up to 50%. The decreasing trend in TP was partly attributed to a decrease in the grassed area and concomitant decrease in DRP load, while the increasing trend in TN was partly explained by accelerated mineralisation of organic matter. According to the latest trend analysis of nutrient losses for 1995−2016 by Räike et al. (2020), flow-normalised TP export from Finnish rivers showed a decreasing trend in that 20-year period. However, different water protection measures to reduce nutrient inputs were not reflected in the actual TP export, indicating that diffuse P loads, originating especially from agriculture, did not decrease in the 20-year period to 2016 (Räike et al. 2020).

1.3. Role of drainage route in phosphorus export

Phosphorus is transported from agricultural land to water via the following key hydrological transfer pathways (Haygarth and Sharpley 2000):

- as overland flow (laterally over the soil surface)
- as interflow (laterally below the soil surface)
- as matrix flow (vertical movement downward)
- as preferential flow (vertical movement along biopores, cracks and fissures).

The significance of different hydrological pathways for P losses depends on *e.g.* antecedent moisture, cultivation and management practices, rainfall intensity and duration, soil type and topography (Heathwaite and Dils 2000). It also depends on redox conditions, drainage system design, and hydrological and climate variables (King et al. 2015). Surface runoff, defined in this thesis as lateral water movement above and below the soil surface, is usually considered to be the primary pathway for P losses, in contrast to N losses. Phosphorus losses in matrix flow through mineral soil profiles are usually relatively small, due to effective P retention by P-poor subsoil with high sorption capacity (*e.g.* Heathwaite and Dils 2000, King et al. 2015). Preferential flow along continuous macropores or cracks and fissures with insufficient water-soil interaction accounts for the elevated P concentrations and high P losses recorded following tile drainage of different soils, especially fine-textured soils (King et al. 2015). Compared with the surface runoff pathway, the subsurface drainflow may be equally important for DRP losses and may even be the main pathway for both PP and TP export from clay soils under cereals (Uusitalo et al. 2018). A higher proportion of TP is generally transported as PP from arable land under cereal cropping, especially from clayey soils sensitive to erosion (Pietiläinen and Rekolainen 1991, Sharpley et al. 1992, Uusitalo et al. 2001). However, no-till has been shown to increase the potential risk of DRP losses (Muukkonen et al. 2007, 2009, King et al. 2015, Uusitalo et al. 2018). Moreover, DRP is often the prominent or predominant P form in losses from grasslands at a lower risk of erosion (Turtola and Jaakkola 1995, Turtola and Kemppainen 1998, Heathwaite and Dils 2000, Uusi-Kämppä and Heinonen-Tanski 2008, Järvenranta et al. 2014). Järvenranta et al. (2014) found that about 90% of TP from grass pasture was transported as DRP in surface runoff generated by melting snow and that snowmelt comprised on average 34% of total annual runoff.

In Finland, snowfall constitutes a considerable proportion of total annual precipitation and soils are annually subjected to a winter frost period. During the snowmelt period, the average spring discharge varies from 100 mm to 200 mm, comprising about 80% of the maximum snow water equivalent and 30–50% of total annual discharge (Vakkilainen 2009). Discharge peaks are typically caused by snowmelt in the north of the country and by autumn rainfall in the south (Vakkilainen 2009). The majority of P loading typically occurs outside the growing season, during the short-term snowmelt period in spring with high runoff potential and during heavy rainfall events in autumn (Puustinen et al. 2007, Räike et al. 2020). The infiltration pathway may be effectively blocked by the ice-filled pores of the frozen zone in freezing soil in wintertime (Miller 1980). Consequently, surface runoff is generated by limited infiltration of melt water into frozen soil during the snowmelt period (*e.g.* Saarijärvi et al. 2007). Dilute snowmelt water, with an increased water-to-soil ratio as a result of large water volume, also extracts P from soil surface layers (Yli-Halla et al. 1995, Yli-Halla and Hartikainen 1996), and transports DRP originating from decaying plant residues.

Close proximity between waterways and artificial drainage systems increases the hydrological connectivity between agricultural land and watercourses, and thus may also accelerate delivery of nutrients to recipient water bodies. Due to excessive wetness, the majority of Finnish fields are artificially drained (Puustinen et al. 1994). Surface- and subsurface-drained land represented 19% and 67%, respectively, of the total agricultural area used in 2013, and only about 14% of the agricultural area in Finland is cultivated without local drainage (Tike 2014). However, different kinds of drainage problems are common, affecting 44% of farmland, and *e.g.* in the spring, about 10% of fields experience flooding problems (Puustinen et al. 1994). Generally, Finnish fields are characterised by proximity to waterways. At national scale, one-third of fields are located next to inland waterways and around 70% of fields are within 300 m of the shoreline of waterways, including lakes, rivers and main ditches (Peltonen-Sainio et al. 2015).

1.4. Role of vegetation in phosphorus losses

Aboveground vegetation, including root and litter layers, can promote the formation of water-stable aggregates, reduce surface flow velocity, enhance the soil infiltration capacity and protect the soil surface from erosion, especially on sloping fields (Jackson et al. 2000, Jobbágy and Jackson 2001, Gyssels et al. 2005). Hence, vegetated buffer zones established between agricultural fields and surface water have been shown to achieve up to 98% reductions in erosion, with simultaneous reductions of 27–46% in TP losses and 54–73% in TN losses (Dillaha et al. 1989, Magette et al. 1989, Dorioz et al. 2006). Vegetated buffer zones have also used successfully for removing particles and PP from agricultural surface runoff under boreal conditions (Syversen 2002, Uusi-Kämppä 2005). However, buffer zones are less effective or even ineffective in reducing DRP losses, especially during the non-growing season in cold regions (Uusi-Kämppä 2005). It has been found that mean annual DRP losses in surface runoff can be up to 70% higher from a buffer zone under natural vegetation than from a buffer zone under annually harvested grass or even from a cultivated clayey field without a buffer zone (Uusi-Kämppä 2005).

During biological cycling, P, N and carbon (C) are translocated or concentrated from deeper soil layers to the topsoil and, on average, >50% of global P and C are found in the upper 30 cm of soil, reflecting plant activity (Jackson et al. 2000, Jobbágy and Jackson 2001). However, decaying plant residues and litter may also become a source of nutrients. Freezing-thawing cycles and drying of plant materials accelerate the release of P (Timmons et al. 1970, Bechmann et al. 2005, Roberson et al. 2007). Thus the elevated DRP concentrations in surface runoff water originate partly from P release from plant residues (Dillaha et al. 1989, Uusi-Kämppä et al. 2000, Dorioz et al. 2006, Uusi-Kämppä et al. 2012). More recently, P release from vegetation in buffer zones or from cover crops has received increasing attention, especially in cold climates (*e.g.* Liu et al. 2014, 2019, Hille et al. 2019).

1.5. Typical features of Finnish agriculture

1.5.1. Grasslands in Finland

Utilised agricultural area (2.3 million ha) constitutes 7.5% of total land area in Finland, of which cereals and grasslands (including about 10% fallow) occupy 47% and 45%, respectively. Pastures comprise approximately 5% of the total area of grasslands. Grasslands occupy an even higher proportion, on average 67%, of the agricultural area in the Finnish inland provinces (South Savo, North Savo and North Karelia), whereas cereals are the dominant crop in southern and southwestern Finland (OSF 2019). Agriculture on the west coast of Finland (North Ostrobothnia) and in east-central Finland (North Savo) is dominated by grass production with dairy and beef cattle, while pork and poultry production are typical agricultural enterprises in south-western and western Finland (Luke/Statistics 2019a, b, c). The plough layer of agricultural soils in southern Finland is characterised by clayey texture, whereas medium-textured mineral soils are common in central and western parts of the country. Coarse-textured mineral soils and glacial tills are typical in eastern, western and northern Finland, while the western and northern parts of Finland are also characterised by organic soils (Lilja et al. 2006, Keskinen et al. 2016, Lemola et al. 2018).

Grasslands are a diverse group even across the Nordic countries, ranging from natural to intensively cultivated grasslands. Finland has no natural grasslands and minor areas of semi-natural grasslands, mostly in coastal areas (Helgadóttir et al. 2014). In Finland, grassland-based dairy production is intense and is the most important agricultural sector in terms of contribution to gross economic return. The Finnish climate is suitable for grass production, and grass silage production with high grass yield per hectare and high digestibility makes it possible to produce milk profitably. Timothy (*Phleum pratense* L.) and meadow fescue (*Festuca pratensis* Huds.) are the most common forage species in Finnish grassland, typically used as a mixture. Potential grass dry matter (DM) yield in Finnish grass experiments can be as high as 9000−12000 kg DM ha^{-1} yr^{-1}, achieved with 200−250 kg N ha^{-1} yr^{-1}. The yields are typically lower on farm level, with a median value of 5500 kg DM ha^{-1} yr^{-1}, and N-fertilisation intensity also tends to be lower (Virkajärvi et al. 2015). Grass swards are typically harvested two or three times per season, with split fertiliser doses for the different cuts. Due to a decrease in ley productivity over time, silage production is typically based on short-term rotational grass leys, where perennial swards are part of the crop rotation and leys are ploughed down at a mean age of 4.4 years, followed by cereal as a cover crop or for whole-crop silage (Virkajärvi et al. 2015).

On-farm manures are an essential component of grass-dominated production systems, but also pose the risk of potential environmental impacts, including gaseous emissions and nutrient losses though runoff and leaching. Using whole-farm balances, it is possible to estimate the nutrient loading potential from animal production systems to the environment in the long-term. Virtanen and Nousiainen (2005) reported mean (± SD) whole-farm balances of 12 ± 7.2 kg P ha^{-1} and 109 ± 41 kg N ha^{-1} for Finnish dairy farms (n = 319) in 2002, with an average animal density of 0.88 (0.25−2.03) livestock units (LSU) ha^{-1} and milk production of about 7600 kg cow^{-1} yr^{-1}. More recently, Kajava and Sairanen (2019) reported higher milk production and animal density for larger conventional dairy farms (n = 9) in east-central Finland, with median values of 10000 ± 900 kg cow^{-1} yr^{-1} and 0.9 ± 0.25 LSU ha^{-1}, and whole-farm balances of 9.5 kg P ha^{-1} and 118 kg N ha^{-1}. Direct comparison between different production systems is difficult, due to lack of information for pig and poultry farming, but dairy farming is reported to be showing a decreasing trend in the whole-farm balance for P (Puustinen et al. 2019). Thus far, due to relatively low livestock density (in LSU ha^{-1}) in grass silage-based dairy farming, the area under cultivation has generally been sufficient for dairy slurry spreading area on farm level (Virkajärvi et al. 2015). However, ongoing structural changes in the Finnish agricultural sector are moving farm and herd size towards larger units (Virkajärvi et al. 2015, Lehtonen et al. 2017).

1.5.2. Phosphorus fertilisation of grasslands

The Finnish agri-environmental support scheme implemented in 1995, upon Finland's accession to the EU, is the main tool used for reducing the environmental impacts of agriculture, particularly on water quality. During the periods 2007−2013 and 2014−2020, the support scheme encompassed 93% and 87% of Finnish farms, respectively (Kauppila et al. 2017). Participating farms commit to complying with P application limits. While farm commitment to the agri-environmental support scheme is still high and covers 94% of all arable area, some of the largest broiler and pig farms have stayed outside the present scheme (Kauppila et al. 2017), and this new development will probably contribute to increased P loading potential in future. Outside the agri-environmental support scheme, application of mineral P fertilisers in a five-year period may not exceed 325 kg P ha^{-1} in agriculture and 560 kg P ha^{-1} in horticulture, *i.e.* 65 and 112 kg P ha^{-1} yr^{-1}, respectively (Ministry of Agriculture and Forestry, decree 5/16). Farm animal manures are not regarded as fertiliser products and are not regulated within this decree (Maa- ja metsätalousministeriö 2008). Application of farm animal manure is restricted to 170 kg TN ha^{-1} per year by the EU Nitrates Directive (91/676/EEC), which also indirectly limits the amount and timing of P fertilisation. Annual P fertilisation is based on recommendations derived from a soil P test (P_{Ac}) involving extraction with acid ammonium acetate at pH 4.65 (Vuorinen and Mäkitie 1955). Phosphorus fertility classes are set by P_{Ac} values in a seven-grade classification system ranging from poor (≤1.3−3.0 mg P_{Ac} l^{-1} soil) to excessive (≥20−50 mg P_{Ac} l^{-1} soil), which can be adjusted further based on soil texture and organic matter content, as described *e.g.* by Peltovuori (1999). In Finland, average concentrations of soil P_{Ac} varied between 9.2 mg l^{-1} and 25.3 mg l^{-1} over the administrative regions in 2005−2009, with the mean of 13.0 mg l^{-1} for the whole country (Lemola et al. 2018).

In Finland, annual sales of inorganic P fertilisers increased sharply in the early 1960s, peaked at 35 kg ha^{-1} in 1975 and remained almost unchanged until the early 1990s. After this, annual sales displayed a downward trend (Yli-Halla et al. 2001), decreasing from 20 kg ha^{-1} in 1994/95 (Tike 2010) to 6.0 kg ha^{-1} in 2013/14 (Tike 2014) and 5.5 kg ha^{-1} in 2017/18 (Luke/Statistics 2018). Unlike inorganic P fertiliser use during 1985−2005, use of manure P remained at a fairly constant level (about 10 kg P ha^{-1}), making up around one-third of total P use in the mid-1980s and around half during 1997−2005 (Uusitalo et al. 2007). At present, farm manure contributes 60% of all P used as fertiliser in agriculture (Marttinen et al. 2018), and is evenly applied to Finnish cultivated fields to meet the P requirement of plants (8.6 kg P ha^{-1}) (Ylivainio et al. 2015). The maximum amount of P fertiliser used for annual or perennial leys ranges from 5 kg ha^{-1} with a soil P class of good to 40 kg ha^{-1} with a soil P class of poor, and from 11 kg ha^{-1} to 46 kg ha^{-1} with annual yield level of at least 7500 kg dry matter (DM) ha^{-1} (Finnish Food Authority 2019).

For Finnish grasslands, cattle slurry application rate is typically 20−40 t ha^{-1} yr^{-1} in one or two applications, and the slurry typically supplies 10−20 kg P ha^{-1}, 60−120 kg N ha^{-1} and 58−116 kg potassium (K) ha^{-1} (Virkajärvi et al. 2015). The slurry is usually applied for the first silage cut in May and the second in June, together with inorganic N fertiliser supplements. In cereal and milk production, solid manure makes up about one-fifth of applied manure, the rest being slurry. Solid manure is applied with a broadcast spreader, whereas an average of 42%, 30% and 28% of slurry is applied using injection, band spreading/trailing shoe and broadcast spreader techniques, respectively (Luke/Statistics 2019d).

1.6. Phosphorus in agricultural soils

1.6.1. Phosphorus forms in soil

On a global scale, the TP content in arable soils typically ranges from 500 mg kg^{-1} to 800 mg kg^{-1}, with the highest concentrations prevailing in the upper A horizon (Stevenson and Cole 1999). The average TP concentration in Finnish agricultural soils is 570−760 mg kg^{-1} (Peltovuori 2006). In minerals soils, around 25−60% of TP occurs in organic forms, but the proportion can be up to 90% in peat soils (Kaila 1963, Condron et al. 2005, Soinne et al. 2011). Phosphorus bound to organic forms in microbial biomass usually constitutes 2−5% of organic P in cultivated soil (Stevenson and Cole 1999). Soil P is often partitioned into P in soil solution, which is described as readily available and replenished from a labile pool (labile P, defined as being in equilibrium with that in soil solution) and non-labile P (defined as equilibrating very slowly) (Pierzynski et al. 2005). In relatively weakly weathered mineral soils in Finland, P reserves are commonly determined by sequential extraction using the Chang and Jackson (1957) fractionation procedure modified by Hartikainen (1979). In that procedure, soil inorganic P pools are partitioned into loosely bound, aluminium (Al), iron (Fe) and calcium (Ca) -bound P fractions, extracted with NH_4Cl, NH_4F, NaOH and H_2SO_4 solutions, respectively. A substantial part of inorganic TP in arable soils still exists as primary apatite. In the plough layer, fertiliser P is bound to hydrated oxides of Al and Fe (Kaila 1964, Hartikainen 1979, Peltovuori et al. 2002, Saarela et al. 2003, Soinne et al. 2011). Based on Finnish fertilisation experiments established at 24 sites in the period 1977−1981, Saarela et al. (2003) estimated that the combined Al- and Fe-bound P fraction in mineral topsoil had increased by 300 kg P ha^{-1} since the early 1960s, and was 600 kg P ha^{-1} higher than in virgin soils. Redox conditions have an indirect effect on P solubility, with the Fe-bound P fraction being susceptible to release. Under anaerobic conditions upon soil flooding or in sediment, ferric iron (Fe^{3+}) is reduced to ferrous iron (Fe^{2+}), with concomitant P mobilisation to the overlying water. The lowering of P sorption capacity is attributed to iron sulphite (FeS) precipitation, which removes Fe^{2+} to be potentially re-oxidised to Fe^{3+} (Ponnamperuma 1972, Wetzel 1983, Correll 1998).

1.6.2. Phosphorus sorption-desorption in soils

On soils with high P-binding capacity, which are generally rich in hydrous oxides of Al or Fe or high in Ca activity, a large part of applied fertiliser P is retained to mineral phases and converted to less plant-available form (Syers et al. 2008). The optimum P concentration in the soil solution for plants is >0.2 mg l^{-1}, but the value typically varies from <0.01 mg P l^{-1} in P-deficient soils to 1.0 mg P l^{-1} in well-fertilised soils, and can be up to 7−8 mg P l^{-1} directly after fertilisation (Pierzynski et al. 2005). Only 15−25% of applied fertiliser P is recovered by field-grown crops in the year of application, but the recovery rate is typically greater, ranging from 50% to 90% in some agroecosystems (Syers et al. 2008).

Sorption-desorption reactions are regarded as the main mechanism controlling the P concentration in the soil solution. Phosphorus in the soil solution is reversibly equilibrated through solution-to-solid phase by sorption-desorption reactions. After fertiliser or manure application, the increase in the P concentration of the soil solution favours sorption from the soil solution into the solid phase. Through plant uptake or increasing water volume, the P concentration in the soil solution is lowered, enhancing desorption from the solid phase (*e.g.* Hartikainen 2009b). Orthophosphate is specifically adsorbed through a ligand exchange mechanism (chemisorption). Depending on pH, the orthophosphate anion displaces water (H_2O) or hydroyxl (HO^-) groups that are coordinated to metal atoms at the surfaces of Al and Fe oxides and hydrous oxides (Hingston et al. 1967, Rajan et al. 1974). Thus the surface charge of minerals becomes more negative with continuing adsorption. Bonds formed with adsorbed P include two types of chemical bonds, more labile monodentate bonds and less labile bidentate bonds (Pierzynski et al. 2005, Hartikainen 2009b). The sorption reaction is initially rapid, followed by a progressively kinetically slower reaction (>40 h) (Ryden and Syers 1975). Diffusive penetration of P into solid soil components is a slow reaction and occluded P is converted to a less labile form with more limited bioavailability (Willett et al. 1988, Chardon and Blaauw 1998). In terms of nonspecific adsorption, negatively charged anions such as phosphate are sorbed onto positively charged surfaces of the hydroxyl ion created by protonation (Iyamuremye and Dick 1996). Some organic P species are also strongly retained in soil, at the same sites as orthophosphate, by ligand exchange (Condron et al. 2005). Phosphorus sorption decreases with increasing pH and saturation of P sorption sites, and with decreasing ionic strength and soil-solution ratio (*e.g.* Ryden and Syers 1975, Hartikainen 1981, Yli-Halla and Hartikainen 1996, Hartikainen 2009b). Soil particles eroded from the P-rich topsoil are also subjected to desorbing conditions when they are transported to watercourses (Koski-Vähälä and Hartikainen 2001, Yli-Halla et al. 2002).

The DRP concentration in surface runoff has been shown to be closely related to soil P status, and increases with increasing soil P status (*e.g.* Sharpley 1995, Turtola and Yli-Halla 1999). The effective depth of the surface soil layer that interacts with rainfall and runoff is shallow (0.1−3.7 cm), but it increases with an increase in rainfall intensity and soil slope (Sharpley 1985). There is a tendency for P accumulation in the soil surface layer over years in perennial leys, pastures and no-till soils (Saarela et al. 2004, Muukkonen et al. 2007, 2009, Saarela and Vuorinen 2010, Järvenranta et al. 2014, Uusitalo et al. 2018). In addition to indirect losses from soil legacy P, direct P losses occur from recently applied P fertilisers and manures, especially from grasslands where P sources are surface-applied (Hart et al. 2004).

1.6.3. Development of soil phosphorus status

Along with the decreasing trend in P fertiliser use in recent decades, mean annual P balance has decreased from about 30 kg P ha^{-1} in 1985−1990 to stabilise at less than 10 kg P ha^{-1} at the start of this century (Uusitalo et al. 2007). It was 5.8 kg P ha^{-1} in 2017, with the highest balances detected in Ostrobothnia, South Bothnia and North Savo (Luke/Statistics 2018). There was a considerable increase in soil P_{Ac} from the early 1960s to the late 1970s, followed by a moderate rise through the 1980s and early 1990s (Yli-Halla et al. 2001, Uusitalo et al. 2007). Based on data collected from the national soil monitoring programme, Keskinen et al. (2016) reported an increasing trend in P_{Ac} concentration between 1974 and 2009 for the plough layer of clay, fine mineral and mull soils with an organic matter (OM) content of 20−40%. For coarse soils, P_{Ac} increased until 1998 in general and then began to decrease, while there was no clear trend in P_{Ac} in peat soils (OM > 40%). In 2009, mean P_{Ac} was highest for coarse soils (13.4 mg l^{-1}; n = 173) and lowest for mull soils (9.5 mg l^{-1}; n = 37). At an equal initial P_{Ac} level of 10 mg l^{-1}, an increase in mean P_{Ac} was found for all cropping systems. In 2009, mean P_{Ac} values were 10.60, 10.64 and 13.04 mg l^{-1} for perennial cropland, crop rotation and annual cropland, respectively. In cropping systems with a higher initial P_{Ac} level, mean P_{Ac} decreased, with perennial cropland being associated with the largest decline (Keskinen et al. 2016). A downward trend in plant-available P in grasslands, as a result of national regulations governing P fertilisation, is also suggested by recent results from long-term experiments in Canada, Finland, France, Germany and Switzerland (Mustonen et al. 2014, Messiga et al. 2015, Virkajärvi et al. 2016, Ohm et al. 2017). For cereals and grasses, a positive response to P fertilisation is not likely to occur above a P_{Ac} concentration of 6, 10 and 15 mg l^{-1} in clay, coarse-textured and organic soils, respectively (Valkama et al.

2011, 2015), which justifies lowering the P concentration in soils with P status above these values.

1.7. Objectives of the thesis

Despite grasslands occupying a substantial proportion of the total Finnish agricultural area, P losses from grasslands to inland waters have received relatively little attention in research. There are some published P loss estimates for perennial leys under Finnish climatic conditions (Turtola and Jaakkola 1995, Turtola and Kemppainen 1998, Uusi-Kämppä and Heinonen-Tanski 2008, Puustinen et al. 2005, 2007) and for soils under pasture (Järvenranta et al. 2014). However, P loss estimates for coarse-textured grassland soils are scarce and catchment-scale data are still completely lacking. In the Finnish water quality monitoring programme, small agricultural monitoring catchments are dominated by cereal cultivation (Vagstad et al. 2001). Taking into account characteristics of cultivation systems, soil properties and the effects of vegetation, P losses from agricultural land under perennial grasslands can be expected to differ from P losses from arable land under cereal cropping. The general aim of this thesis was thus to examine the role of perennial vegetation in P dynamics in the soil-plant-water continuum and P losses from grasslands under boreal conditions, in which silage production is based on short-term rotational grass leys. A second aim was to improve understanding of the P cycle in boreal grasslands, and their susceptibility to P losses. Regarding grasslands, better knowledge of the amount and seasonality of P losses and the ratios of DRP and PP to TP in these losses would improve modelling outcomes. It would also enable integration of results obtained at experimental plot scale with results obtained at catchment scale, which could lead to more effective mitigation options to meet P reduction targets, including under changing climate conditions in future.

Specific objectives of the work described in this thesis were:

- To estimate the potential contribution of perennial vegetation to P losses (Paper I) and the effect of harvesting perennial ley on P losses in surface runoff (unpublished data).
- To estimate the soil erosion rate for grasslands, using total suspended solids (TSS), and to determine the relative contribution of PP to TP in surface runoff from grasslands on coarse-textured mineral soils (Papers II and III).
- To quantify P losses and study seasonal and inter-annual variations in P losses from grassland at the small catchment scale in a grassland-based intensive dairy production system typical for east-central Finland during a five-year monitoring period (Paper III).

2. Materials and method

2.1. Study sites

This thesis presents the results from three studies together with unpublished data, which are referred to hereafter as the "Paper I–III" and "this thesis", respectively. The field studies were conducted in Jokioinen in south-western Finland (Paper I), in Maaninka in North Savo, east-central Finland (Paper II, this thesis), on the premises of Natural Resources Institute Finland (Luke) and at water monitoring sites established in 2010 in the catchment area of Lake Kirmanjärvi in North Savo (Paper III) (Figure 1). The small (3.2 km^2) agricultural and forested monitoring catchment studied in Paper III contains intensive dairy production on areas including grasslands, cereals and forest, representing typical agricultural areas in east-central Finland.

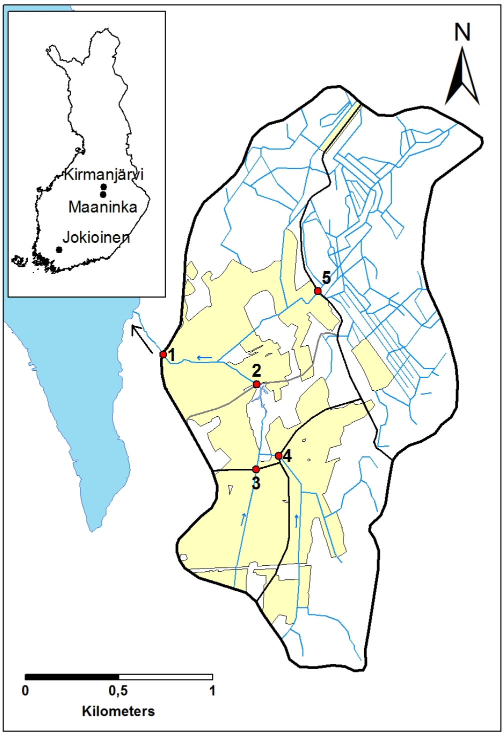


Figure 1. Insert: Map showing the location of the experimental sites: Jokioinen in south-western Finland (Paper I), Maaninka in east-central Finland (Paper II, this thesis) and a 3.2 km^2 water monitoring catchment near Lake Kirmanjärvi in east-central Finland (Paper III). Main image: Based on dominant land use, the monitoring catchment (1) contained three sub-catchments, agricultural (3), mixed (4) and forested (5). Water from the agricultural and mixed sub-catchments discharges through a constructed wetland (2) into Lake Kirmanjärvi. Numbers represent monitoring areas and red points sampling sites. Yellow shaded areas represent land under cultivation with subsurface pipe drainage systems, and blue lines represent main open ditches. Diagram by Samuli Heikkinen (Luke).

The Maaninka field sites were under fertilised silage grass leys in a short-term ley rotation, whereas the Jokioinen sites represented long-term unfertilised grasslands. In Jokioinen, the study was conducted in grass buffer zones (18 m × 10 m) established in 2002 or 1991, 3 or 14 years before sampling, between cultivated fields and the main ditch receiving agricultural surface runoff from a source field area. Prior to establishment of the buffer zones, the soil had been fertilised and tilled annually for several decades, but since buffer zone establishment no tillage or fertilisation has been performed. Some of these buffer zone sites were included in a long-term field experiment by the Natural Resources Institute Finland in Jokioinen, in which surface and subsurface water were collected to 30 cm depth (*e.g.* Uusi-Kämppä and Yläranta 1992, Uusi-Kämppä and Jauhiainen 2010). The differently managed 3-year-old and 14-year-old grass buffer zones are referred to in this thesis as "young" and "old", respectively. They were harvested by (i) grazing ("grazed"), (ii) cutting the grass and removing the residues ("harvested") or (iii) not cutting and not removing the vegetation ("natural"). The vegetation consisted of:

- A multispecies community of perennial grasses at the old natural buffer zone sites. One of the natural sites also included a thin stand of shrubs and is referred to hereafter as the old (woody) natural site.
- Mainly timothy and meadow fescue at the young and old harvested sites.
- Mainly timothy and meadow fescue at the young and old grazed buffer zone sites. Average grazing intensity was 72 cow grazing days ha^{-1} yr^{-1} in 2003, 234 cow grazing days ha^{-1} yr^{-1} in 2004 and 128 cow grazing days ha^{-1} yr^{-1} in 2005.

For the same grass buffer zone sites, results from other studies conducted in parallel with paper I have been reported previously, by *e.g.* Rasa et al. (2007a, b) and Räty et al. (2010).

Mean values of selected average soil properties at the experimental sites are summarised in Table 1. For the unfertilised grass buffer zones at Jokioinen, the organic carbon (OC) content in the surface layer (0−5 cm) was within the range 2.5−5.1% (0.22−0.38 total N-%) and the P_{Ac} value was 4.9−15.4 mg l^{-1} (mean 10.0 mg l^{-1}), with the values decreasing with depth and being highest for the old natural sites (Paper I). For the Maaninka fertilised grass leys on different soil types, the OC and P_{Ac} values were within the range 2.9−6.5% (0.13−0.43 total N-%) and 6.2−10.3 mg l^{-1}, respectively (Paper II, this thesis). Under the Finnish soil P classification system, the uppermost soil layers were classified as satisfactory at all experimental sites (*e.g.* Peltovuori 1999). The topsoil consists of clay and very fine sandy loam at Maaninka, while the Jokioinen topsoil consists of silty clay. Soil TP during the study averaged about 1160 mg kg^{-1} at Jokioinen and 1600 mg kg^{-1} at Maaninka. The potential cation exchange capacity (CEC_{pot}, including titratable acidity) at Jokioinen was about 28 cmol(+) kg^{-1}, with a soil base saturation of 85%. At Maaninka, the CEC_{pot} was about 25 cmol(+) kg^{-1} (40%) on clay soil and 11 cmol(+) kg^{-1} (66%) on very fine sandy loam. Typically, the fine clay fraction consists of illite, chlorite, smectite, vermiculite and amorphous material, while the content of feldspar and quartz increases with increasing particle size (Sippola 1974). The silty clay soil at Jokioinen was classified as a Vertic Stagnic Cambisol and the very fine sandy loam at Maaninka as a Humic Dystric Regosol (IUSS Working Group WRB 2007).

The formation of the geologically young soils of Finland was influenced by the last Weichsel glacial period, which ended about 11 500 years ago, and by subsequent evolutionary stages of the Baltic Sea and post-glacial land upheaval. Glacial till is a common soil type in Finland, and soils are relatively rich in poorly weathered materials (Hartikainen 2009a). Owing to the parent materials (granite, quartzites) and the absence of calcareous material, Finnish soils are naturally acidic (Reuter et al. 2008). In addition, surface soils (0−30 cm) are rich in OC in a European comparison (Aksoy et al. 2016). Due to their young pedogenetic age, Finnish soils tend to be mostly relatively weakly developed, while many different soil-forming processes are proceeding. Human-influenced pedogenetic processes have been identified for clayey soils, due *e.g.* to artificial drainage permitting soils to dry out to greater depth (Yli-Halla et al. 2009). On including soil moisture and translocation of clay particles in the classification (World Reference Base for soil Resources WRB), Yli-Halla and Nyborg (2013) classified cultivated clay soils as Vertic Endogleyic Luvic Stagnosols, or Luvic Gleysols in wet depressions, silt soils as Stagnic Regosols, fine sand soils with deeper layers rich in clay as Endogleyic Luvic Planosols, and very fine sand or fine-sandy moraine soils as Endogleyic Cambisols. Most soils have a cryic temperature regime in Soil Taxonomy, characterised by low soil temperature (mean summer temperature below 15 ^{o}C), delaying pedogenesis (Yli-Halla and Mokma 1998). Clayey soils in southern Finland are also considered to have an aquic moisture regime (Yli-Halla and Mokma 2001).

Table 1. Mean value of selected properties of the top 0-5 cm layer in experimental soils at the Jokioinen and Maaninka sites.

Location	**Study**	**Texture**[a]	**Clay**	**Silt**	**Sand**	**pH**[b]	**OC**[c]	$\mathbf{P_{Ac}}$[d]
			%				**%**	**mg l^{-1}**
Jokioinen	Paper I	Silty clay	51	42	7	5.5	5.4	10.0
Maaninka	Paper II	Very fine sandy loam	8	37	55	5.8	2.9	10.3
Maaninka	Thesis	Clay	43	36	21	5.3	6.5	6.2

[a]Soil texture determined by the pipette method (Elonen 1971) and classified according to the U.S. Department of Agriculture (USDA) system, using particle size limit 0.002–0.063 mm for silt.
[b]pH measured in soil-water suspension (1:2.5 v:v).
[c]Organic carbon (OC) determined by dry combustion.
[d]Soil test P (P_{Ac}) extracted with 0.5 M acid ammonium acetate at pH 4.65 (Vuorinen and Mäkitie 1955).

2.2. Weather conditions

Finland falls within the boreal zone, with cold winters, relatively warm summers and moderate precipitation in all seasons. Finland has an intermediate climate, showing characteristics of both maritime and continental climate. Due to the geographical position, there is large temporal and spatial variation in weather conditions, with weather type tending to vary rapidly, especially in winter (Kersalo and Pirinen 2009). During the normal period 1971−2000, the duration of the growing season ranged from 101 to 195 days and the sum of effective temperature ranged from 447 to 1433 ^{o}C (Kersalo and Pirinen 2009). In the latest normal period 1981−2010, mean annual temperature varied from -1.9 to 6.5 ^{o}C, decreasing from the southwest to the northeast (Pirinen et al. 2012). The warmest month of the year is typically July (mean monthly temperature 11.2 to 17.8 ^{o}C) and the coldest months are January and February (mean monthly temperature -2.2 to -14.5 ^{o}C). The average number of cold days per year with minimum temperature <-10

°C varies from 9 to 118, with the maximum snow depth occurring in March. Annual precipitation exceeds annual evapotranspiration and mean annual precipitation varies from 433 to 768 mm, increasing from the northwest to the southeast. The lowest monthly precipitation (20−43 mm) typically occurs in late winter (February-March) and spring (April), while the rainiest months (54−92 mm) are July and August (Pirinen et al. 2012). In southwest Finland less than one-third of precipitation falls as snow, whereas snow constitutes 40−50% of precipitation elsewhere in Finland and up to 60% in the far north (Kersalo and Pirinen 2009).

For description of the different study periods, meteorological data (daily air temperature, precipitation and snow depth) were obtained from the Finnish Meteorological Institute's observation stations located in Jokioinen in southwestern Finland and in Maaninka and Vieremä Kaarakkala in east-eastern Finland. Long-term averages for the normal period 1981–2010 were taken from Pirinen et al. (2012).

2.3. Experiments, sampling and measurements

In Paper I, the potential contribution of perennial vegetation to P losses was estimated indirectly by determining changes in the nutrient content of aboveground vegetation in the differently managed grass buffer zones. Plant samples were collected on six occasions, with five replicates per occasion, between May 2005 and April 2006, using a quadrat frame method (0.5 m × 0.5 m) and clipping the vegetation to a height of 2 cm. These samples were used in examining temporal variations in the amount and nutrient content of aboveground biomasses, and in attempts to explain the commonly observed increase in DRP concentration in surface runoff water flowing through vegetated buffer zones. In addition to the aboveground vegetation, the amount and nutrient content of belowground parts of vegetation were determined by taking core samples (200 cm^3) at depths of 0−5 and 5−10 cm, with five replicates, from each grass site in May in 2005. Living roots were not separated from what is collectively referred to hereafter as "belowground biomass". The root growth dynamics of perennial grasses were recorded by the minirhizotron-microvideo camera technique to 40 cm soil depth over one growing season until the following spring, with three replicates and imaging on five occasions per site. Mean and standard deviation (±SD) were calculated from the replicates taken within the non-replicated grass sites. The standard error of the mean (SEM), standard error of the difference (SED) and Student's T-test least significant difference (LSD) at $p \leq 0.05$ were calculated over the sampling times according to each site, using the GLM procedure in the SAS software (version 9.1; SAS Institute Inc., Cary, NC, USA).

In Paper II, the susceptibility of overwintering regrowth of a perennial ley to deliver P losses was assessed in surface runoff induced by applying simulated snowmelt to grass sods. Soil losses from grasslands in the short-term ley rotation were also estimated. The study, with a randomised complete block design in four replicates, included untreated control and non-recurrent biochar addition with three increasing levels (10, 20 and 40 t ha^{-1}), in conjunction with cattle slurry (40 t ha^{-1}). Excluding the application year 2011 for the TP, DRP and dissolved organic C (DOC) concentrations with the highest biochar addition, there were no statistically significant differences between treatments in the TP, DRP, DOC and total suspended solids (TSS) concentrations in simulated runoff outflow. The three-year field experiment was started in 2011 in a grass field seeded in 2010 with timothy (cv. Tuure, seed rate 20−25 kg ha^{-1}). The leys were harvested in two cuts per season. In 2011−2013, the study area was fertilised with NPK compound fertiliser by surface application, divided into two doses, the first in May (100 kg N ha^{-1}, 15 kg P ha^{-1}, 25 kg K ha^{-1}) and the second in June-July (100 kg N ha^{-1}, 0 kg P ha^{-1}, 28 kg K ha^{-1}). Grasses were expected to be naturally prepared for winter prior to lifting. Grass sod storage, simulated snowmelt and sampling were carried out as follows (Saarijärvi and Virkajärvi 2010):

Undisturbed topsoil layers, including aboveground and belowground biomasses (0.35 m × 1.0 m × 0.05 m), were cut by a modified turf grass cutter and lifted at the end of the growing season, on October 25−27 in 2011, on October 17 in 2012 and on November 4−6 in 2013, depending on autumn weather conditions. On the same occasion, small grass-soil layers were taken from each plot for vegetation and soil sampling. To estimate the amount of regrowth remaining in the field, residues were collected by clipping the vegetation to the soil surface (in an area of about 0.33 m × 0.33 m). The lifted grass sods were laid on impermeable sheets, wrapped in plastic covers and stored outside under prevailing winter conditions until simulated snowmelt was applied in January-March. The simulation of snowmelt to induce surface runoff was conducted in a non-heated room, where the indoor temperature tended to follow the temperature in the open air but remained slightly above zero degrees. The frozen grass sods were placed at an average slope of 5%, and snow collected from adjacent fields was added in two equal portions of 15 kg inside transparent plastic frames. During the seven-day simulation period, the melting process was controlled by infrared heaters and the grass sods were not allowed to thaw until the latter addition. The replicates were repositioned for different simulation runs. Snowmelt-induced surface runoff volume was collected and weighed, and one composite water sample was taken from each individual grass sod and stored at 4 ^{o}C until analysis.

In Paper III, the amount and inter-annual variation in P, N, DOC and TSS losses were quantified for the small (3.2 km^2) agricultural and forested catchment during a five-year monitoring period (2011−2015). The relative contribution of DRP to TP was also estimated. The study catchment contained sub-catchments, which were classified as agricultural, mixed and forested according to their main land use (Figure 1, Table 2). This thesis primarily focuses on the results from the agricultural sub-catchment. The whole catchment included mixed land uses of forestry, ley and cereal farming, grazing land, farmyards and buildings, whereas in the agricultural and mixed sub-catchments, the cultivated area was mainly under ley-cereal rotations. Owing to the short-term ley rotation, there were annual changes in the proportions of grasslands and cereals in the monitoring areas. Over half of the agricultural land was under grassland (52%), the rest being under spring cereals (48%), and around 60% of the cultivated area was under autumn ploughing. In the plough layer, the average P_{Ac} values were comparable to the range of means (8.7−11.4 mg P l^{-1}) reported by Lemola et al. (2018) for mineral soils in North Savo in 2005−2009.

At all measurement sites, instrument shelters included water samplers, rechargeable batteries for an uninterrupted power supply and data loggers, and heating cables were used in sampling and pressure probe tubes. The flow rate was monitored continuously using an acoustic flow meter or a combination of a pressure probe and a V-notch weir. Water samples were taken using an automated programmable sampler or manually during periods with lower flow rate (17−30 per site and year). The relationships between TSS, DOC and TP, PP and DRP concentrations in water samples were assessed using a simple linear regression analysis (II, III, this thesis), and the *p*-values were presented for the slopes of the regression lines.

Table 2. Description of the water monitoring areas in a 3.2 km^2 agricultural and forested monitoring catchment (whole catchment) and its agricultural, mixed and forested sub-catchments.

Water monitoring area	Site[a]	Area, km^2	Field-%
Agricultural sub-catchment	3	0.27	93
Mixed sub-catchment	4	0.65	36
Forested sub-catchment	5	1.02	4
Whole catchment	1	3.20	32

[a]Numbering of sampling sites in the monitoring areas according to Figure 1.

This thesis also presents results from an unpublished study ("this thesis"), in which the effect of changing the timing of the second silage cut on P and N losses from grassland was studied, using the same simulated snowmelt method as in Paper II. This study is reported here for the first time, but a part of the results have previously been presented in a Finnish abstract (Räty et al. 2015). The two-year field experiment was started in 2012 in a grass field established in 2010 with a mixture of timothy (cv. Tuukka, seed rate 12 kg ha^{-1}) and meadow fescue (cv. Ilmari, seed rate 10 kg ha^{-1}), using cereals as the cover crop. The study area was fertilised according to Finnish recommendations as described for Paper II. The leys were harvested twice per growing season to 7 cm stubble height, by a plot grass harvester. The treatments, each with four replicates, were arranged in a randomised complete block design on grass plots of 3.75 m^2 (1.5 m × 2.5 m) separately in both years. The six treatments included different harvesting times of the second cut, which resulted in differing amounts of overwintering regrowth remaining in the field over winter. For the first cut, the harvesting time was the same for all treatments. The different harvesting times of the second cut were set at intervals of 14 days starting from a treatment "harvest 1", which represented the conventional harvest time of second-cut silage in the study region. The treatments also included an unharvested treatment, where the second cut was not harvested. For the simulation, grass sods were lifted on October 15 in 2012 and on October 30−31 in 2013. Grass sod storage, simulated snowmelt and sampling were carried out as in Paper II. Analysis of variance (ANOVA) was carried out using the MIXED procedure in the SAS software (version 9.3; SAS Institute Inc., Cary, NC, USA). Treatments were considered to be fixed effects and replicates random effects. Years were analysed separately. Pairwise comparisons were performed by Tukey's test. Statistical significance was set at $p \leq 0.05$.

2.4. Methods

The methods used in Paper I−III and in the unpublished study ("this thesis") are summarised in Tables 3−5. For a more detailed description, see Papers I−III.

Table 3. Summary of methods used in analysis of soil samples.

Method	Description	Reference	Study
Particle-size distribution	Pipette and sedimentation method.	Elonen (1971)	I, II, thesis
Potential cation exchange capacity (CEC_{pot})	Extraction with 1.0 M CH_3COONH_4 at pH 7.0 (1:5 w:v). Concentrations of Ca, Mg, K and Na measured by ICP-OES and exchangeable acidity by titration.		I, II, thesis
pH	Measured in soil-water suspension (1:2.5 v:v)	Vuorinen and Mäkitie (1955)	I, II
Soil test P (P_{Ac})	Extraction with 0.5 M CH_3COONH_4, 0.5 M CH_3COOH (1:10 w:v, 1 h) at pH 4.65. Measurement with a Skalar autoanalyser.	Vuorinen and Mäkitie (1955)	I, II, III, thesis
Total organic C	Dry combustion (Leco® CHN 900 or TruMac® CN analyser).		I, II, thesis
Total N (TN)	Dry combustion (Leco® CHN 900 or TruMac® CN analyser).		I, II, thesis
Total P (TP)	Extraction with concentrated H_2SO_4, H_2O_2 and HF. Measurement at a wavelength of 882 nm by spectrophotometer.	Bowman (1988)	I, II

Table 4. Summary of methods used in analysis of plant samples.

Method	Description	Reference	Study
Dry matter (DM) content	Drying at 60 °C for 48 h.		I, II, thesis
Secondary dry matter (DM)	Drying at 105 °C for 16 h.		I, II, thesis
Total P (TP)	Thermal oxidation at 500 °C, dissolution in a mixture of $HCl-HNO_3-H_2O$ acid. Measurement at 882 nm by spectrophotometer (Perkin-Elmer Lambda).	Jones (2001)	I
Total P (TP)	Wet-acid digestion with concentrated HNO_3 and 30% H_2O_2. Measurement with ICP-OES.	Huang and Schulte (1985)	II, thesis
Water-extractable P fractions	Dried and milled sample was extracted with water (1:50 w:v, 18 h). Shaking, filtration (2.0-µm, 589[3] blue ribbon filter paper, Schleicher & Schuell, GmbH).		I
Water-extractable total P (TP)	P determination after oxidation with $K_2S_2O_8$ and H_2SO_4 in an autoclave (100 kPa, 120°C, 30 min).		I
Water-extractable inorganic P	Precipitation by dilute H_2SO_4 (filtration) before P determination.		I
Water-extractable organic P	Water-extractable total P (TP) - Water-extractable inorganic P.		I
P determination	Colorimetrically with a molybdenum blue method, and measurement at 882 nm by spectrophotometer (Perkin-Elmer Lambda).	Murphy and Riley (1962)	
Total organic C	Dry combustion (Leco® CHN 900 analyser).		I
Total N (TN)	Dry combustion (Leco® CHN 900 or TruMac® CN analyser).		I, II, thesis
Root growth			
Root growth dynamic	Minirhizotron-microvideo camera technique		I
Separation of roots and litter from soil	Hydropneumatic elutriation system	Smucker et al. (1982)	I

Table 5. Summary of methods used in analysis of water samples.

Method	Description	Reference	Study
Total P (TP)	Determined in unfiltered sample, oxidation with $K_2S_2O_8$ and H_2SO_4 in an autoclave (200 kPa, 30 min).	SFS 3026, mod.[a]	II, III, thesis
Dissolved reactive P (DRP)	Determined in filtered sample (0.2-µm, Nuclepore® polycarbonate, Whatman International Ltd.)	SFS 3025, mod.[a]	II, III, thesis
P (PO_4-P) determination	Colorimetrically with a molybdenum blue method, and measurement at 880 nm by a Skalar autoanalyser.	Murphy and Riley (1962)	
Particulate P (PP)	Total P (TP) - Dissolved reactive P (DRP)		II, III, thesis
Total N (TN)	Determined in unfiltered sample, oxidation with $K_2S_2O_8$ and NaOH in an autoclave (200 kPa, 30 min). TN was determined colorimetrically as NO_3-N.	SFS 3031, mod.[a]	II, III, thesis
Ammonium-N (NH_4-N)	Determined in filtered sample (0.2-µm, Nuclepore® polycarbonate, Whatman International Ltd.)	SFS 3032, mod.[a]	II, III, thesis
Nitrate-N (NO_3-N)	Determined in filtered sample (0.2-µm, Nuclepore® polycarbonate, Whatman International Ltd.)	SFS 3030, mod.[a]	II, III, thesis
Dissolved organic N (DON)	Total N – Dissolved inorganic N (NO_3-N, NH_4-N)		
NO_3-N determination	Colorimetrically with cadmium reduction method in a Cu-Cd column, measurement at 540 nm by a Skalar autoanalyser.		
NH_4-N determination	Colorimetrically based on a Berthelot reaction in alkaline solution, measurement at 660 nm by a Skalar autoanalyser.		
Total suspended solids (TSS)	Filtration and weighing solid material remained on a filter (1.6 µm, Munktell glass microfibre filter).	SFS-EN 872, mod.[b]	II, III, thesis
Dissolved organic C (DOC)	Determined in filtered sample (1.2 µm, Munktell glass microfiber filter), measurement by a Shimadzu TOC-V CSH.		II, III
Water monitoring			
Flow rate measurement	Continuously with an acoustic flow meter (Starflow Ultrasonic Doppler Instrument, Model 6526) or a pressure probe (STS DL/N Series 70) and a V-notch weir.		III
Water sampling	Automatically with a programmable sampler (Endress+Hauser AG, Liquiport 2000 RPT20) or manually as grab samples.		III

[a]In a method modification, preservation with acid was not applied.
[b]In a method modification, a smaller volume was used and TSS was not determined within 24 hours.

3. Results and discussion

3.1. Nutrient content in biomass

3.1.1. Aboveground biomass

Shorter days, lower solar radiation and temperature slow down the growth of grass leys in late summer (Helgadóttir et al. 2014, Virkajärvi et al. 2015). Average daily growth rate is relatively small in the third cut and especially after the last cut, which takes place in by mid-September at the latest (Hyrkäs et al. 2016). Despite slow regrowth potential, the grass continues to grow after the harvesting season, taking up nutrients from the soil and reducing the risk of nutrient leaching losses from the root zone. This regrowth is left in the field and contains a differing stock of nutrients, which may be released to the environment. With future climate change, the thermal growing season is predicted to be extended at high latitudes (Peltonen-Sainio et al. 2009, Helgadóttir et al. 2014), which might result in an increase in the amount of regrowth left in the field during the overwintering period.

In the studies described in this thesis, in October-November there was a noticeable amount of overwintering regrowth in the unfertilised grass buffer zones (Paper I) and at the grass ley sites that had been fertilised in the previous growing season for the first (100−15−25 kg ha^{-1} NPK) and second (100−0−28 kg ha^{-1} NPK) silage cuts (II, this thesis). At the silage grass ley sites in 2011−2013, the amount of autumn regrowth of timothy grass after the second cut in July-August varied from 1024 to 1419 kg DM ha^{-1}, with a TP content of 2.5−3.3 kg ha^{-1} and a TN content of 18−23 kg ha^{-1} (Paper II). In the harvest timing experiment in 2012−2013 (this thesis), the timing of the harvest varied between July and September for the second cut, which resulted in differing amounts of overwintering regrowth of timothy and meadow fescue grass mixture (Table 6). The regrowth amount varied from about 660 to 2400 kg DM ha^{-1} in the harvested treatments, with a TP content of 1.4−4.6 kg ha^{-1} and a TN content of 9.8−42 kg ha^{-1}. The unharvested treatment, where the second cut was not harvested, produced average growth of 3790 kg DM ha^{-1}, with a content of 5.9 kg TP ha^{-1} and 48 kg TN ha^{-1}. These results illustrate that P and N are still taken up until the late growing season at different kinds of grass sites and incorporated into aboveground biomass of autumn regrowth.

Table 6. Average dry matter (DM) yield of autumn regrowth (kg ha^{-1}), and total phosphorus (TP) and total nitrogen (TN) content in the regrowth during 2012−2013, which examined the effect of different harvest timing of the second cut on DM yield, TP and TN content of regrowth. Means (n = 4) with different letters differ significantly at $p \leq 0.05$ (Tukey's test).

Year	Treatment	Date of 2nd cut	Amount of regrowth	TP content	TN content
			kg DM ha^{-1}	kg ha^{-1}	
2012	*Unharvested	-	3596^{a}	6.5^{a}	43^{a}
	**Harvest 1	July 31	1758^{b}	3.9^{b}	26^{b}
	Harvest 2	Aug 14	1433^{bc}	3.4^{bc}	25^{b}
	Harvest 3	Aug 28	942^{bc}	2.2^{bcd}	17^{bc}
	Harvest 4	Sept 11	871^{bc}	1.9^{cd}	15^{bc}
	Harvest 5	Sept 25	769^{c}	1.4^{d}	9.8^{c}
Average			1562	3.24	22.6
SEM			219	0.40	2.64
p-value			<0.001	<0.001	<0.001
2013	Unharvested	-	3989^{a}	5.3^{a}	54^{a}
	Harvest 1	July 16	2011^{bc}	3.5^{abc}	35^{ab}
	Harvest 2	July 30	2400^{ab}	4.6^{ab}	42^{ab}
	Harvest 3	Aug 13	1272^{cd}	2.6^{bc}	26^{ab}
	Harvest 4	Aug 27	1012de	2.4^{c}	22^{b}
	Harvest 5	Sept 10	664^{e}	1.6^{c}	16^{b}
Average			1891	3.32	32.4
SEM			.	0.55	7.04
p-value			<0.001	<0.001	0.007

*Unharvested treatment = the second cut was not harvested.
**Harvested treatments 1−5 = each treatment had a different time for the second cut. The second cut was harvested at intervals of 14 days starting from the first harvested treatment (Harvest 1).
*** SEM denotes standard error of the mean.

Accumulated grass biomass is also an issue in unfertilised buffer zones, which are a specific type of grassland established along watercourses. The average DM yield in differently managed grass buffer zones peaked in August (2120–6270 kg ha^{-1}), with a content of 3.1−8.7 kg TP ha^{-1} and 24−65 kg TN ha^{-1} (Paper I). The growth consisted of mixed herbaceous plant species, with the dominant species being timothy and meadow fescue. The yield was comparable to that reported for plots on mineral soils receiving no N fertiliser in Finnish fertilisation experiments (900−6300 kg DM ha^{-1} yr^{-1}) (Valkama et al. 2016). The entire biomass of 1630−3860 kg DM ha^{-1} in the unharvested natural buffer zone sites remaining in the field over winter contained 2.0−4.1 kg TP ha^{-1} and 24−43 kg TN ha^{-1} (Paper I). The harvested sites produced autumn regrowth of 800−880 kg DM ha^{-1} after the harvest (Paper I), which was mostly lower than at fertilised grass ley sites (Paper II, this thesis). However, the harvested grass buffer zone sites still included about 1.0 kg TP ha^{-1} and 11 kg TN ha^{-1} in late November, and this remained at the sites over winter (Paper I).

The grass buffer zone sites, which were uncultivated and unfertilised for 3 and 14 years after site establishment prior to sampling, showed moderate biomass production, suggesting that the soil had reached relative stability (Paper I). Mean plant-available inorganic P fraction (sum of H_2O-P and $NaHCO_3$-P) averaged 140 mg kg^{-1} in the uppermost soil layer (0–5 cm) of the silty clay soil sites studied (Rasa et al. 2007b). At most buffer zone sites, the soil test P value (5–15 mg l^{-1}) was also higher than the threshold value of 6 mg P_{Ac} l^{-1} for clay soils, above which responses to P fertilisation would not be expected (Valkama et al. 2011). The unfertilised grass sites seemed to contain adequate levels of plant-available nutrients originating from the fertilisation history and the source field area. Organic P turnover is considered to be important, especially under P-limited conditions, when the supply of fertiliser P is unavailable or limited (Stutter et al. 2015), probably resulting in efficient cycling of nutrients within these unfertilised sites.

3.1.2. Belowground biomass

The results showed that the roots tended to be concentrated in the uppermost 10 cm of the old plough layer, averaging 2.5−5.4 roots cm^{-2} in June-August at the grass buffer zone sites (Paper I). At the old (woody) natural site, root numbers gradually decreased with depth down to 40 cm. Large numbers of living roots were also recorded at soil depths of about 20−30 cm at the harvested and grazed grass sites (0.4−5.8 roots cm^{-2}), but above (10−20 cm) and below (30−40 cm) that there were fewer roots, indicating increased mechanical resistance and restricted growth into the soil (Paper I). Compared with the AB horizon (16−38 cm depth), there was a sharp decline in air permeability (from 28×10^{-5} to 9.7×10^{-5} m s^{-1}) deeper in the soil (Bw horizon, 38–45 cm depth), an indication of reduced pore continuity. Simultaneously, the OC content decreased from 2.2 to 0.9% and the bulk density increased from 1.25 to 1.34 g cm^{-3} from the AB to the Bw horizon (Räty et al. 2010). The root growth rate was still high in the latter part of the growing season (Paper I), reflecting growth dynamics typical of perennial and annual grasses in boreal conditions (Pietola and Alakukku 2005, Marjamäki and Pietola 2007). The high root numbers persisting to mid-October suggest that grasses may take up nutrients to some extent even at the end of the growing season (Paper I). Thereafter, there was a distinct decline in root numbers, of on average 85%, between October and early May of the following year (Figure 2). This reflected a high mortality rate during winter and senescence of the aboveground vegetation, resulting in low nutrient uptake capacity of grasses in the spring. Therefore, nutrient removal by herbaceous vegetation uptake is not an important mechanism for mitigating nutrient losses during the spring runoff period.

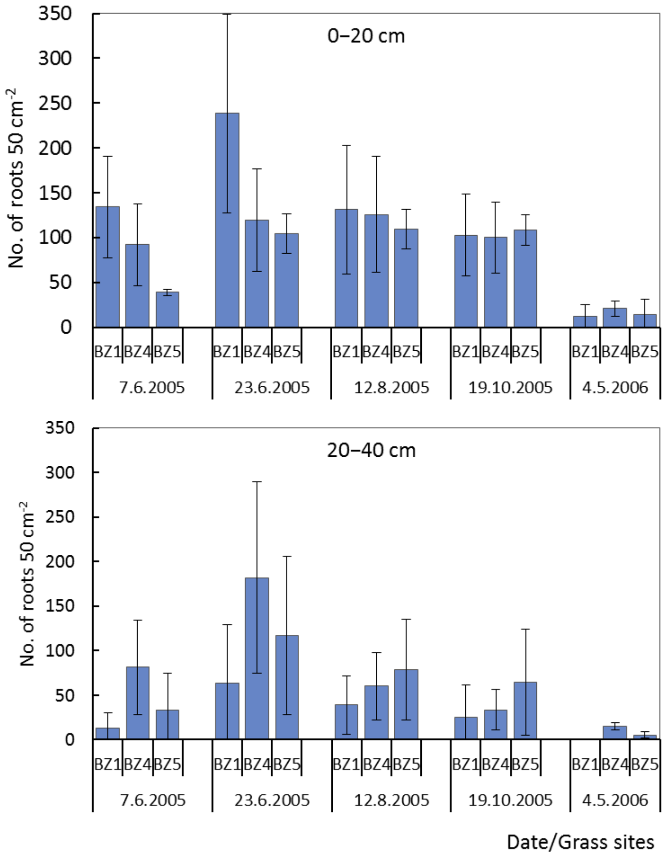


Figure 2. Total root numbers (no. of roots 50 cm^{-2}) recorded by the minirhizotron-microvideo camera technique at a depth of 0–20 cm (upper diagram) and 20–40 cm (lower diagram) in the grass buffer zone (BZ) sites (Paper I). BZ1 = old (woody) natural site, BZ4 = old harvested site, BZ5 = young grazed site. Means and standard deviations (±SD) (n = 3).

In the grass buffer zones, the DM yield of belowground biomass was 2.3- to 6.6-fold higher in the upper 5 cm of soil layer than at 5–10 cm depth (Paper I). The biomass was measured in early May, before aboveground growth had started, and consisted of living roots and senesced herbaceous plant material. Belowground biomass amounted in total to around 20 600 kg DM ha^{-1}, with 270 kg TN ha^{-1} and 7590 kg C ha^{-1}, with the biomass amount and nutrient content being lowest at the old (woody) natural site and highest at the old grazed site (Figure 3). Although the TP content of the belowground plant material was only defined for the uppermost soil layer, it was clearly higher (4.5–20 kg ha^{-1}) than that in the aboveground vegetation. Compared with the abundant aboveground biomass present in August, the results showed major accumulation of belowground biomass at the unfertilised grass sites (Paper I).

In previously published results from Finnish trials on perennial grasses, data on the combined biomass of belowground root and litter and their nutrient content have rarely been included. Comparable results to those found in Paper I were reported by Virkajärvi et al. (1997), who studied sod production with cultivars of common meadow grass (*Poa pratensis*), red fescue (*Festuca rubra*) and common bent (*Agrostis capillaris*) on cut-away peat bog. They found that about 65% of belowground biomass was located in the uppermost 0–2 cm soil layer in the second growing year, with the amount varying from about 1.0 to 2.5 g DM at 0–2 cm depth (the cross-section area of sample was 40.7 cm^2). The biomass consisted of living roots and partially decomposed plant material. Based on the amount of belowground biomass reported by Virkajärvi et al. (1997), the high belowground to aboveground biomass ratio on silty clay soil in Paper I can be explained by thatch/litter accumulation in the long-term. Perennial leys have a beneficial effect and greater potential for soil C sequestration, especially compared with cereal monoculture rotations (*e.g.* Soussana et al. 2010, Börjesson et al. 2018). By providing soil C inputs through high accumulation of belowground biomass, unploughed unfertilised grasslands used as buffer zones or grazed grasslands might have the potential to act as a C sink over the longer-term.

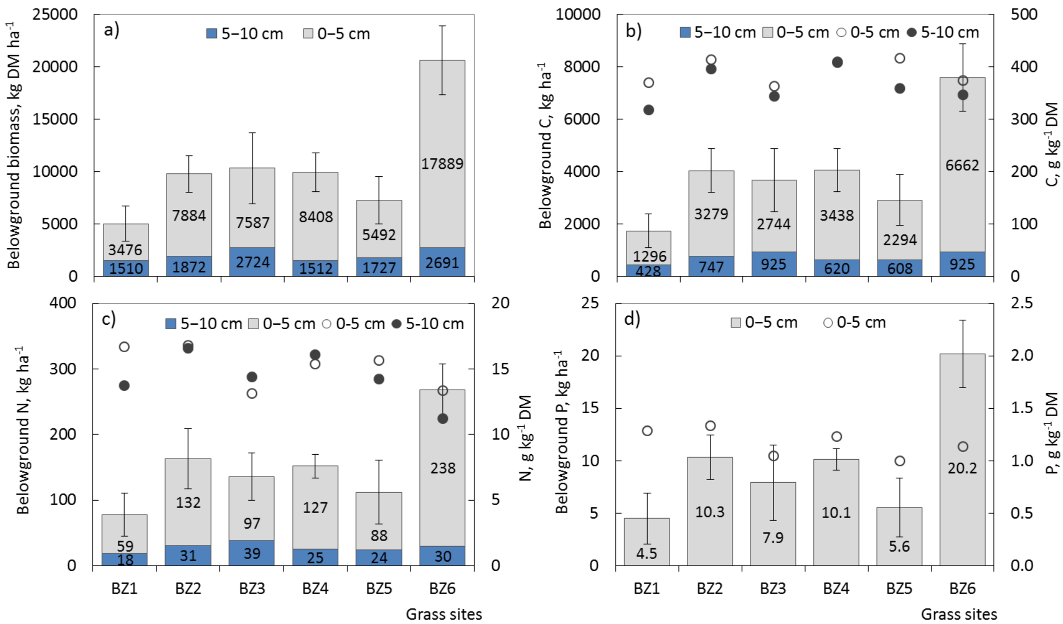


Figure 3. a) Mean dry matter (DM) biomass of living roots and litter (kg DM ha^{-1}), here referred to as belowground biomass, b) content of carbon (C), c) nitrogen (N) and d) phosphorus (P) in biomass (kg ha^{-1}) and mean concentrations of these nutrients (g kg^{-1} DM) at a depth of 0–5 cm (grey bars) and 5–10 cm (blue bars) at differently managed grass buffer zone (BZ) sites (Paper I). Mean C, N and P concentrations are presented as scatter points on the second y-axis. Unfilled points represent the 0–5 cm depth and filled points the 5–10 cm depth. BZ1 = old (woody) natural site, BZ2 = old natural site, BZ3 = young harvested site, BZ4 = old harvested site, BZ5 = young grazed site and BZ6 = old grazed site. The means and the standard deviations (±SD) were calculated from five replicates and SD is presented for the 0–5 cm soil layer.

In grasslands, abundant aboveground and belowground biomass affects soil structural and hydrological properties, which in turn affect transport of nutrients and eroded soil material. At the same old grazed grass site as in Paper I, Räty et al. (2010) noticed a decrease in soil resistance to compression, but it was compensated for by greater rebound capacity. Therefore, organic grass residues may protect the soil surface from management-related structural deterioration (*e.g.* grazing) that might have a restrictive influence on water infiltration. On the other hand, grasslands may exhibit organic matter-related soil water repellency, diminishing water infiltration and potentially promoting preferential flow and surface runoff pathways (Rasa et al. 2007a). In addition, pore space clogging by plant roots can cause a reduction in hydraulic conductivity (Pietola et al. 2005, Bodner et al. 2008). Surface runoff is reported to comprise a larger proportion of total annual runoff during grass ley growing years than in the establishment year (Turtola and Kemppainen 1998), increasing the susceptibility of grasslands to DRP losses.

3.2. Plant-derived risk of phosphorus losses

3.2.1. Effect of amount of autumn growth on nutrient losses

Potentially water-transportable nutrients in plant material after first frost

Some nutrients can be released to water from aboveground plant material that is left in the field over winter. For clipped fresh grass biomass (ryegrass, alfalfa), only on average 1−3% of plant TP is in water-extractable form, but freezing, freezing-thawing cycles and drying of grass tissue can significantly increase the solubility of P in water (Bechmann et al. 2005, Roberson et al. 2007). After several repeated freeze-thaw cycles, all the P in grass biomass may be converted to water-extractable form (Bechmann et al. 2005). When plant cells have been disrupted, dehydrated and ruptured by freezing or severe water stress, P is more readily leached from these plant cells (Timmons et al. 1970, White 1973). Most TP in aboveground biomass at the different grass buffer zone sites was extractable with water (79–93%), as determined on dried samples (Paper I). Water-extractable inorganic P averaged 84% of plant TP, while the rest was considered to comprise organic P compounds (Paper I). The water-extractable proportion of biomass is strongly affected by pre-treatment procedure, increasing in the order: untreated fresh plant material < frozen ≤ frozen/thawed < dried (Roberson et al. 2007). The substantial water-extractable percentage can be accounted for in part by the combination of vigorous pre-treatment and extraction procedure (Paper I). Consequently, it can be described as the potential amount of P that can be released to water from plant material.

Total P and TN content in aboveground biomass remained relatively unchanged throughout the winter months (Paper I). However, high TP and TN reductions in the stand were found to have occurred between the samplings in October and November, taking place before and after the first frost occurrences. The reduction varied from 0.5−6.1 kg ha^{-1} for TP and was up to 30 kg ha^{-1} for TN. This coincided with a reduction in DM yield of on average 30%. Under field conditions, the biomass was subjected to natural freezing and thawing prior to sampling in November, resulting in enhanced P solubility (Paper I). Due to the adaptation of perennials to the prevailing climate conditions, some of the TP and TN reductions observed were most probably consequences of remobilisation and translocation of nutrients from shoot to roots. In perennial forages, reserve-N compounds are accumulated in roots and root nodules, and endogenous N reserves play a role in forage regrowth and stress tolerance (Volenec et al. 1996). Partala et al. (2001) studied the uptake of fertiliser N by reed canarygrass using a labelled ^{15}N technique and observed reallocation to belowground plant parts, corresponding to a 3−13 percentage-point increase in recovery during autumn. On the other hand, concurrent with the cessation in aboveground biomass production, part of the pool of root-bound nutrients is released with root decomposition, as shown earlier. Even if P losses were overestimated by the vegetation-based indirect approach, the additional information provided in this thesis supports the claim that vegetation can be source of appreciable P release to surface runoff water.

Some of the P released is most likely adsorbed into the surface soil, affecting the composition of runoff indirectly through accumulation and desorption to water. Following leaching by rainfall or snowmelt water, some plant P may directly contribute to losses in surface runoff. These conclusions are supported by Uusi-Kämppä and Jauhiainen (2010), who measured high DRP losses (0.5−0.9 kg ha^{-1}) in spring surface runoff flowing through the same grass buffer zone sites as used in Paper I. For the same grass buffer zone sites, the equilibrium P concentration (EPC) values, representing the point of no P net sorption or desorption (Taylor and Kunishi 1971), were obtained from P desorption-sorption isotherms. The EPC values varied from 0.2 to 2.3 mg P l^{-1} for the 0–2.5 cm soil depth and from 0.1 to 0.5 mg P l^{-1} for the 2.5−5 cm soil depth in these silty clay soils (Rasa et al. 2007b). Relative to the DRP concentration measured by Uusi-Kämppä and Jauhiainen (2010), the results indicate that surface soil at unharvested natural sites may act as source of P, releasing P to runoff water. The increase in EPC values was due to P enrichment originating from plant residues and source field area. In addition, P sorption may be decreased and P mobility increased by organic compounds such as organic acids and humic substances (Iyamuremye and Dick 1996, Daly et al. 2001, Haynes and Mokolobate 2001), increasing the tendency for P release from the surface soils of grasslands with the generally high OM content.

Nutrient losses during simulated spring snowmelt

The above-mentioned indirect approach was complemented with data from the simulated snowmelt-induced surface runoff study, to estimate the susceptibility of overwintering regrowth to deliver P to runoff water interacting with soil in the spring. When the grass sods were lifted in late autumn (October-November), including the topmost soil surface layer with litter and roots, the grasses were naturally prepared for winter prior to the snowmelt simulation treatments. In the harvest timing experiment on clay soil (this thesis), the mean TP and DRP concentrations in simulated runoff outflow were 0.23 mg l^{-1} and 0.13 mg l^{-1} in 2012 over the treatments, respectively. In 2013, higher mean concentrations of 0.46 mg l^{-1} and 0.17 mg l^{-1} for TP and DRP, respectively, were recorded. The DRP constituted 59% and 37% of runoff TP concentration in 2012 and 2013, respectively. As for the mean TN concentration, an increase from 3.4 mg l^{-1} in 2012 to 11.5 mg l^{-1} in 2013 was observed. Of the runoff TN concentration, dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON) made up 70% and 30%, respectively, in 2012 and 78% and 22%, respectively, in 2013, with nitrate-N (NO_3-N) typically comprising the major part of DIN.

In 2012, the harvest timing treatments (this thesis), with the different amounts of autumn regrowth present, had no significant effect on TP and DRP concentrations or mass losses. The different treatments produced similar average TP losses of 0.02 g m^{-2} in surface runoff outflow, which is approximately equivalent to 0.17 kg ha^{-1} (Figure 4), making up 2.8−11% of TP incorporated into autumn regrowth. This was consistent with Miller et al. (2015), who studied the effect of stubble height relative to depth of overland flow and reported no mowing treatment effects on reduction of P and sediment losses from native rangeland sites under simulated runoff. Roberson et al. (2007) compared full growth and removed alfalfa treatments in the field under simulated and natural runoff and found increased P and sediment losses from the removed alfalfa treatment, where the alfalfa was mown to ground level, which they attributed to greater runoff volume and enhanced soil P extraction. Thus the advantages of plant P removal with harvested biomass may be partly counteracted by a vegetation height-induced increase in runoff volume under field conditions. In grasslands, part of the P delivered might also originate from organic residues accumulated on the soil surface, levelling out the advantages of harvesting.

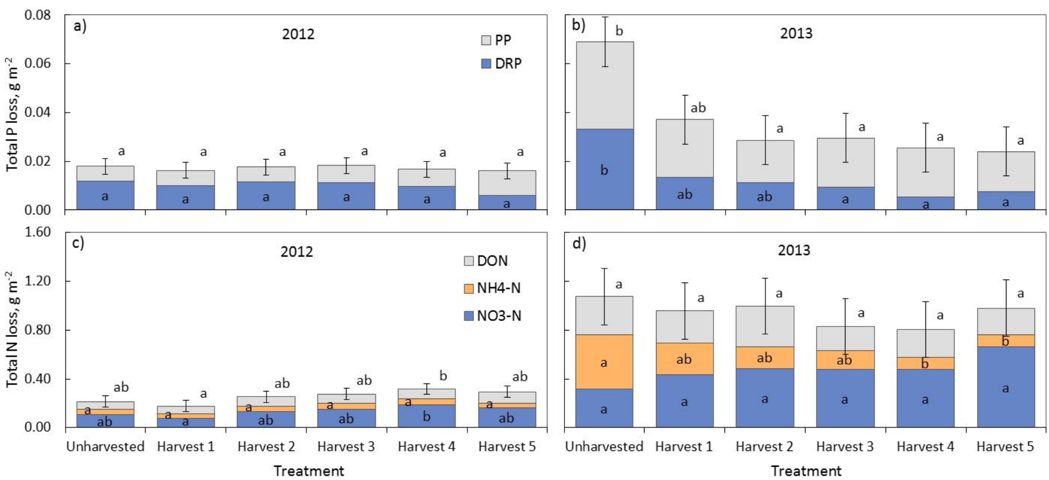


Figure 4. Effect of amount of autumn regrowth, resulting from different harvesting times of the second cut, on phosphorus (P) and nitrogen (N) losses from grass sods under snowmelt simulation (g m^{-2}, n = 4) (this thesis). Total P (TP) losses in surface runoff for grass sods lifted in a) 2012 and b) 2013, and total N (TN) losses for grass sods lifted in c) 2012 and d) 2013. TP is divided into dissolved reactive P (DRP) and particulate P (PP), and TN into nitrate-N (NO_3-N), ammonium-N (NH_4-N) and dissolved organic N (DON). The error bars represent the standard error of the mean for TP and TN. Significant differences ($p \leq 0.05$) in TP and DRP losses for P and TN, NO_3-N and NH_4-N losses for N between treatments in individual years are indicated by different letters.

In 2013, the unharvested treatment produced almost four-fold higher TP losses (0.07 g m^{-2}, equivalent to 0.69 kg ha^{-1}) than observed in 2012 (Figure 4). The unharvested treatment differed significantly ($p \leq 0.05$) from those harvested later (treatments 2−5), in July-September, which averaged 0.03 g TP m^{-2} (equivalent to 0.26 kg TP ha^{-1}). The proportion of DRP to TP tended to increase and, correspondingly, the proportion of PP to TP to decrease, with increasing amount of autumn regrowth. The unharvested and harvested treatments produced nearly four-fold higher TN losses in runoff outflow in 2013 (0.94 g m^{-2}, equivalent to 9.4 kg ha^{-1}) than in 2012 (0.26 g m^{-2}, equivalent to 2.6 kg ha^{-1}). Of the TN, the proportion of NH_4-N tended to increase and the proportion of NO_3-N to decrease with increasing amount of autumn regrowth, especially in 2013. All treatments exhibited higher P losses in 2013 than in 2012 (this thesis). The treatment "harvest 1", representing the conventional harvest time for second-cut silage, produced equal or higher P losses than later harvested treatments. Therefore, the results indicate that the higher P losses were not explained by the effect of delayed harvest time on overwintering under the prevailing conditions. The large amount of autumn regrowth, with the OM accumulated on the soil surface, may enhance plant-derived P losses. At the same time, abundant organic material may restrict the degree of interaction between surface soil and runoff water and consequently, reduce P release to runoff water. Based on the difference in TP losses between unharvested and harvested treatments in 2013, around 0.40 kg TP ha^{-1} can be assumed to originate from plant residues, averaging 11% of regrowth TP. However, prior to lifting the grass sods, some of the plant P might also have leached after the first frost in the field. Overall, these results confirm that vegetation can act as a substantial source of P losses from grassland.

Agricultural soil is also subjected to frost and repeated freezing-thawing cycles. In freezing soils where ice is forming, liquid water flows into the zone of freezing and the soil solution is concentrated (Miller 1980). Consequently, the thickness of the diffuse double layer decreases and the concentration of anions in the diffuse layer increases (Ryden and Syers 1975). Therefore, P sorption is suggested to be enhanced in freezing mineral soils (Soinne and Peltovuori 2005). However, Hinman (1970), Ron Vaz et al. (1994) and Messiga et al. (2010) instead reported enhanced P availability, which they attributed to physical disruption, solubilisation and hydrolysis of soil organic compounds and substances. In grasslands, with a higher OM content, freezing can be assumed to play a more important role in the P cycle than in arable soils under cereal cultivation.

3.2.2. Effect of winter conditions on phosphorus losses

The harvest timing experiment was conducted simultaneously with Paper II, in which the effect of biochar addition on P and N losses from timothy grass was investigated using the same simulated snowmelt-induced surface runoff method. On a very fine sandy loam, on average twofold higher TP concentrations and losses in runoff outflow were observed over the treatments from the grass sods lifted in 2013 (0.63 mg l^{-1}, 40 mg m^{-2}) than in the previous year (0.29 mg l^{-1}, 20 mg m^{-2}) (Paper II). High P concentrations and losses originating from grass sods lifted in the first year (2011) were related to the non-recurrent implementation of treatments in the preceding autumn prior to snowmelt simulations. Overall, a higher proportion of DRP in TP concentration was observed in Paper II (mean 77%) than in the harvest timing experiment (mean 44%) over the treatments and years.

In the simulated snowmelt experiments (Paper II, this thesis), 30 kg of melted snow generated an average runoff volume of around 76 mm. There were no significant differences in the total runoff volume between treatments within the experiment and study year. Thus the higher TP losses were explained by higher P concentrations in surface runoff outflow. For grass sods lifted in 2013, the snowmelt simulation was conducted in January-March 2014. Prior to the simulations, the grass sods were wrapped in plastic covers and stored outside, and snow was allowed to fall on them. During the storage periods, the weather conditions varied significantly, especially in terms of snow depth. In the winters of 2011−2012 and 2012−2013, there was a thick permanent snow cover that melted by late April, as is typical for the region. In contrast, the winter 2013−2014 was characterised by an exceptionally thin and uneven snow cover (Figure 5), with mean minimum daily temperature of -23 ^{o}C and a maximum depth of soil frost of 37 cm in grasslands. In addition, the first snow melted in December, the weather alternated between snowing and melting in the following months, and the snow melted completely already in March. At the small catchment scale, this weather regime produced two damped discharge peaks in two short snowmelt periods, instead of one high discharge peak during the intense spring snowmelt period (Paper III).

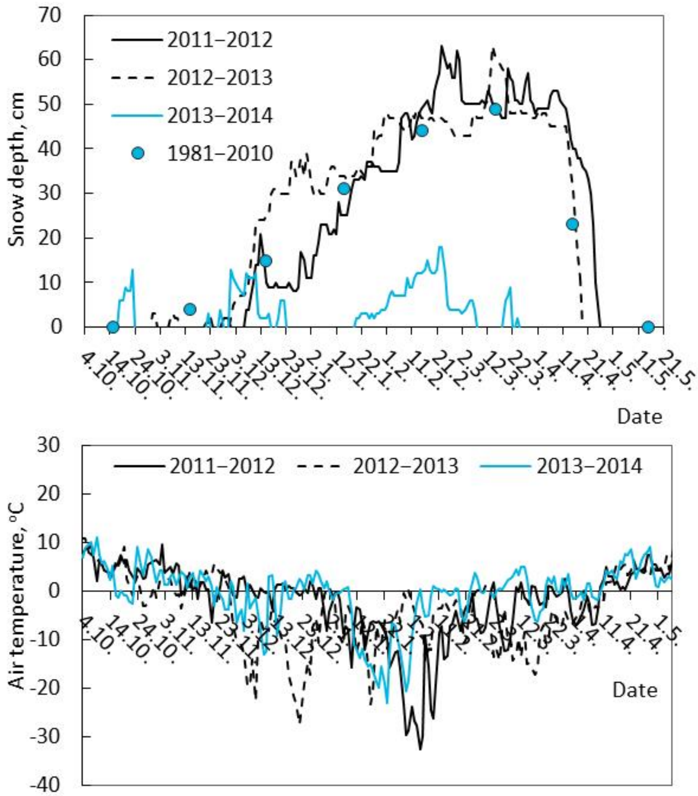


Figure 5. (Upper diagram) Mean daily snow depth (cm) and (lower diagram) mean daily air temperature in the study region during winter 2011–2014. The filled points represent the long-term monthly averages (15th day) of snow depth for the normal meteorological period 1981–2010 (Pirinen et al. 2012).

For grass sods lifted in 2013, the elevated P concentrations and losses in simulated runoff outflow can probably be accounted for the low degree of insulation, as a consequence of the absence of permanent and thick snow cover. Therefore the grasses and the topmost layer of roots and litter were exposed to the repeated freezing and thawing and more severe frost damage, resulting in elevated P concentrations and losses in surface runoff outflow. At the small catchment scale (Paper III), the occasional higher measured P concentrations in early spring runoff can be partly explained by P release from decaying or frost-injured vegetation. These findings are similar to those in many freeze-thaw experiments carried out with different plants and experimental techniques by *e.g.* Bechmann et al. (2005) in the USA, Roberson et al. (2007) in the USA, Uusi-Kämppä et al. (2012) in Finland, Elliot (2013) in Canada and Liu et al. (2014) in Sweden. They report elevated P concentrations in leachate, runoff outflow or drainage water originating from the aboveground biomass after repeated freezing and thawing treatments. Under a changing winter climate, the predicted increase in autumn temperature may decrease the effectiveness of cold acclimation of herbaceous plants (Helgadóttir et al. 2014, Rapacz et al. 2014). Combined with reduced or lack of permanent snow cover, this may enhance the risk of freezing damage to vegetation and, consequently, increase the risk of plant-derived P losses.

3.2.3. Effect of grass species on phosphorus losses

The release of soluble P is also related to plant P status (Sharpley 1981) and the stage of growth or decomposition of the vegetation. For example, it is higher for actively growing vegetation with a higher moisture content (Timmons et al. 1970, White 1973). Susceptibility to P losses and freeze-thaw cycles also depends on plant species or residue types, *e.g.* clover and ryegrass have the high risk of frost-induced P release (Liu et al. 2014, Elliot 2015). In the simulated snowmelt experiments in this thesis (Paper II, this thesis), the TP losses in surface runoff outflow increased with the increase in regrowth TP content over the treatments only for grass sods lifted in autumn 2013 (Figure 6). The results are not entirely consistent with Elliot (2013), who found that the amount of P released from clipped residues during simulated snowmelt was strongly correlated to the P content of the residues and weakly with soil test P. However, the snowmelt simulation experiments included only a few grass species and thus the P concentrations and regrowth biomasses were probably not different enough to reveal a clear relationship between P losses in outflow and regrowth P content. In 2011 and 2012, a thick layer of snow insulated the grass sods from air temperature during the storage period, which may have further weakened the relationship. In late autumn (October-November), grasses were also naturally prepared for winter prior to the simulated snowmelt treatments. In addition, some of the released P was adsorbed into the soil and thus part of the P delivered during freezing-thawing might originate from the soil.

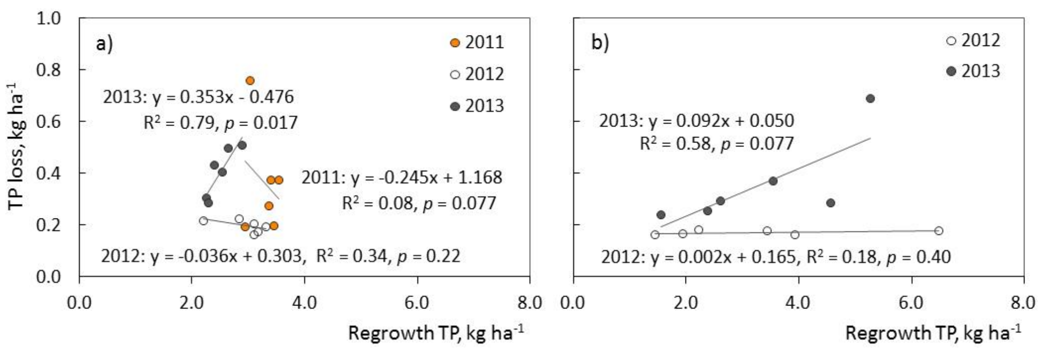


Figure 6. Relationship between total phosphorus (TP) losses in simulated surface runoff outflow (kg ha^{-1}) and TP content (kg ha^{-1}) in vegetation regrowth in different treatments (n = 4) during 2011−2013 in a) Paper II and b) the harvest timing experiment (this thesis).

Soil P mining by harvesting grass grown with zero external P application has been suggested as an effective method for reducing P loading risk (Koopmans et al. 2004, van der Salm et al. 2007). In unfertilised grass buffer zone sites studied in this thesis (Paper I), harvest of 3840–4830 kg DM ha^{-1} in August removed relatively low amounts of nutrients (3.3−4.7 kg TP ha^{-1}, 19−28 kg TN ha^{-1}) when compared with the average P yield of about 27 kg ha^{-1} of fertilised grass leys in the two-cut system, with the high DM yield level (Virkajärvi et al. 2016). Despite this, harvesting of grass sites used as buffer zones is recommended, due to the measured high DRP losses from unharvested treatments. This is supported by the higher P losses observed from the simulated snowmelt experiments in 2013, especially from the unharvested site (this thesis). Different herbaceous plant species could perhaps be utilised for soil P mining in regions with high soil P status and a high risk of P losses, including *e.g.* species with different rooting patterns or higher P assimilation.

3.3. Soil erosion from grasslands

3.3.1. Soil erosion rate

In the Nordic countries, the most important soil erosion agents are meltwater during the snowmelt period and rainfall in autumn, in combination with limited infiltration capacity (Lundekvam and Skøien 1998, Ulén et al. 2012). In terms of the erosive force of rainfall, the main erosion mechanism is related to the impact of raindrops on the soil surface. Therefore, vegetation and plant residues play an important role in absorbing the kinetic energy of falling raindrops transmitted to the soil surface (Aura et al. 2006). In boreal conditions, the importance of snowmelt and autumn rainfall periods for soil particle transport varies both locally and seasonally (Puustinen et al. 2007, Ulén et al. 2012). As regards land use, up to 98% of the variation in erosion rate is explained by the proportion and mean slope of arable land, the proportion of open-ditched fields and the proportions of grassland and ploughed land area (Mansikkaniemi 1982). In the small (3.2 km^2) agricultural and forested catchment studied in this thesis, the mean annual erosion rate (3.4−115 kg ha^{-1}) decreased with an increasing proportion of forest land area in the catchment in the monitoring period 2011−2015 (Paper III).

Aboveground vegetation and roots contribute to erosion control, as topsoil erosion resistance is strongly increased by grasses with a shallow and dense rooting pattern (Gyssels et al. 2005). In flow simulations for an erosion-prone sandy loam, soil detachment rate has been found to decline to a very low level with root density increasing from 0 to 4 kg m^{-3} in the top 8.8 cm soil layer (De Baets et al. 2006). At 5 cm depth in the grass buffer zone sites in this thesis (Paper I), the combined dry mass of living roots and plant debris was two- to nine-fold higher than the threshold value found by De Baets et al. (2006), above which an increase in root density does not result in an additional increase in soil resistance. In the small-scale simulation experiments performed, the mean erosion rate measured as TSS varied from 0.2 to 3.0 kg ha^{-1} (Paper II) and 1.0 to 11 kg ha^{-1} (this thesis), associated with an average total volume of around 76 mm of runoff outflow. Assuming an annual discharge volume of 344 mm on average for the agricultural sub-catchment (Paper III), the estimated annual erosion rate was roughly only 0.8−13 kg ha^{-1} on a very fine sandy loam (Paper II) and 4.5−48 kg ha^{-1} on a clay soil (this thesis). At the small catchment scale, mean annual erosion rate was 115 kg ha^{-1} (46−287 kg ha^{-1} yr^{-1}) from the agricultural sub-catchment with 93% fields, of which grasslands make up at least half the cultivated area (Paper III). The respective mean annual flow-weighted TSS concentration was 34 mg l^{-1} (10−119 mg l^{-1}) in the monitoring period 2011−2015. These observed erosion rates were considerably lower than those in Mansikkaniemi (1982) and Puustinen et al. (2005), who reported mean annual erosion rates of 2000−3000 kg ha^{-1} from arable land on the clayey soils in southwestern Finland. The highest annual erosion rate originating from the agricultural sub-catchment was more comparable with the 470 kg ha^{-1} reported previously for grass leys on a flat experimental field on fine sand (Turtola and Kemppainen 1998) and the 570 kg ha^{-1} reported for a sloping experimental field on clay soil (Puustinen et al. 2005). Thus the protective cover of overwintering regrowth, together with the uppermost layer of belowground biomass, appeared to serve as a protective cover and to play a crucial role in preventing erosion from the grasslands at the study sites.

In the agricultural sub-catchment, the TSS and PP concentrations in water samples did not correlate with daily mean discharge (Paper III). However, based on the large water volume occurring in spring, on average 72% (range 37−92%) of TSS was transported during spring high water period (March-May), whereas while 15% (range 2−48%) was transported in autumn (September-November) and about 6% in summer and winter (Figure 10). The erosion rate varied from around 140 to 290 kg ha^{-1} yr^{-1} in two out of five monitored years, and was otherwise around 50 kg ha^{-1} yr^{-1}. The mean annual erosion rate was 80 kg ha^{-1} (26−192 kg ha^{-1} yr^{-1}) for the whole catchment (Paper III). A relatively small amount of TSS losses is also attributable to the topography of the agricultural land in the catchment, which is rather flat, with most fields having a slope of less than 1.5%. However, direct comparison of the results reported in previous Finnish studies and in the present thesis is difficult, due to possible differences in the method used for measuring erosion rate (evaporation residue method or TSS method). Of the combined total amount of solid materials and dissolved substances, an average of 49% was transported in solute and the remaining 51% in solids in a coastal clayey area of Finland (Mansikkaniemi 1982). In the evaporation residue method, the amount of eroded soil is determined from unfiltered, dried water sample, containing both solid materials and dissolved substances. In grasslands, vegetation significantly reduces soil erosion but may contribute to the transport of dissolved substances, and slurry application may further increase the amount of salts in discharge water. Consequently, use of the evaporation residue method may result in overestimation of erosion rate. The TSS method, where solid material remains on a filter and dissolved salts and organic substances are excluded with the filtered water, should therefore be used in measuring erosion rate from grassland-dominated areas.

3.3.2. Erosion in short-term ley rotation

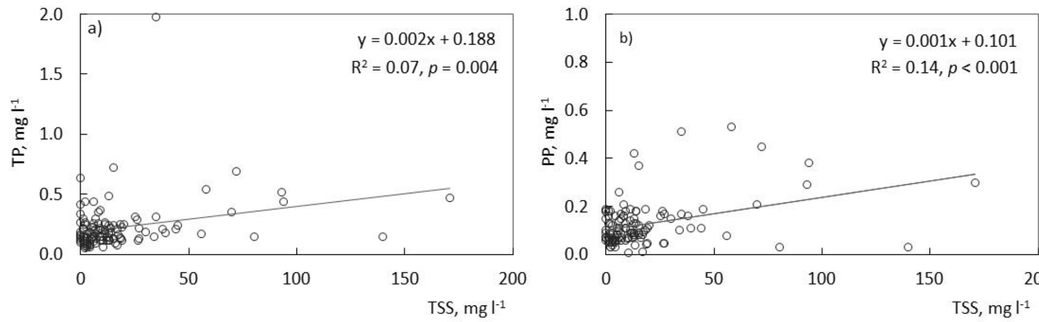
The small-scale simulated snowmelt experiments on partially thawed soil (Paper II, this thesis) probably underestimated the annual erosion rate from grass-covered soil, by not including *e.g.* hydrological differences. The role of hydrology becomes more important with transition from small-scale plot studies to large-scale catchment studies, as catchments exhibit more complexity and heterogeneity (Haygarth et al. 2012). The grass sods used in the simulated snowmelt experiments in this thesis represented well-managed grass leys with dense growth and root systems, and thus the results are representative of relatively dense-growing grass leys. In intensively managed grasslands, however, vegetation does not necessarily provide a complete surface cover against erosion, which is characterised by an episodic and spatially discontinuous pattern (Haygarth et al. 2006). Furthermore, topsoil structure can be locally deteriorated or destroyed by grazing cattle or heavy machinery used in grassland cultivation, contributing to increased surface runoff and particle detachment. At a small catchment scale, as in Paper III, TSS losses were also affected site-specifically by bank erosion, maintenance work on the existing ditch network and overland flow enriched with suspended sediment material along farm tracks.

In the small-scale simulation experiments (Paper II, this thesis), the 1- to 14-fold higher TSS losses (kg ha^{-1}) were found in 2013 than in 2012. This increment might be partly attributable to freeze-thaw induced deterioration of soil structure during the storage period, resulting in an increase in dispersed soil material in simulated outflow. Compared with cereal fields with similar soil OC content, the percentage of water-stable aggregates is higher under permanent grassland (Soinne et al. 2016). However, as a disintegrating force, freezing and thawing may decrease aggregate stability in different soils (Kivisaari 1979, Oztas and Fayetorbay 2003, Kværnø and Øygarden 2006, Edwards 1991, 2013). In particular, it may be more severe on initially unstable silt soils than on structured clayey soils (Kværnø and Øygarden 2006). Moreover, silt clay loams and silt loams are sensitive to water erosion, especially in combination with autumn ploughing (Lundekvam and Skøien 1998). Generally, North Savo is considered to be a region with low soil erodibility (Lilja et al. 2017). Although clayey fields are not common, silty clays and silt loams comprise about 22% of plough layer soil types (Lemola et al. 2018) and these soils are likely to have higher susceptibility to erosion.

In this thesis, the higher mean erosion rate recorded in the agricultural subcatchment than in the simulated snowmelt experiments was partly attributable to the grass-cereal rotation, where part of the grassland area is renewed after autumn ploughing. Of the total Finnish arable area, 22% was bare in winter 2015−2016, while the rest was covered by crop plants (46%, including fallow), plant residues or stubble (18%), catch crops (4%) and conservation tillage (10%). In cereal production, a larger part (79%) of the cultivated area was tilled and/or sown compared with that in dairy production (41%). Of which 40% and 53% was autumn-ploughed in crop and dairy production sectors, respectively. Overall, about 25% and 20% of the Finnish cultivated area in cereal and dairy production, respectively, remains bare over winter (Luke/Statistics 2019d). Although grasslands are clearly less prone to soil losses during growing years, an increase in the proportion of autumn-ploughed land lying bare over winter may result in a substantial increase in erosion rate and PP losses (Turtola and Kemppainen 1998, Puustinen et al. 2005, 2007). From a soil erosion viewpoint, extending the growing years of short-term leys might be advisable. However, due to a decrease in productivity over time, leys are typically re-established at frequent intervals, as ley overseeding is not a commonly used practice to maintain grassland productivity in Finland (Virkajärvi et al. 2015). Thus in short-term ley rotations, nutrient and TSS losses from grasslands should be considered within the whole ley rotation cycle, including establishment and renewal of grass, in combination with the prevailing ploughing practice.

3.3.3. Nature of erosion material on grasslands

In clayey regions of southern Finland, a strong positive linear relationship has been found between online recorded turbidity and the concentrations of TSS, TP and/or PP in water samples originating from agricultural catchments (Valkama et al. 2008, Linjama et al. 2009, Ekholm et al. 2012, Valkama and Ruth 2017). This enables indirect monitoring of P losses by means of sensor-based turbidity monitoring. Villa et al. (2019) used data from 108 Swedish stream monitoring sites to evaluate the use of turbidity as a surrogate for TSS and TP concentrations. They found that site-specific turbidity-TSS and turbidity-TP relationships were both significant for 73% of the sites and were stronger in catchments with a larger proportion of agricultural land and high TP concentrations. In the agricultural sub-catchment with a very high percentage of fields examined in this thesis (Paper III), there was only a weak linear relationship between concentrations of TSS and P concentrations in water samples from the monitoring areas in 2011–2015 once two samples with exceptionally high TSS concentrations were excluded (Figure 7). Additionally, there was year-to-year variation in the relationships between TSS and P, and DOC and P (TP, PP, DRP), indicating changes in the nature and origin of eroded material. In most years, however, the TP concentration was more closely correlated with DOC than with TSS.



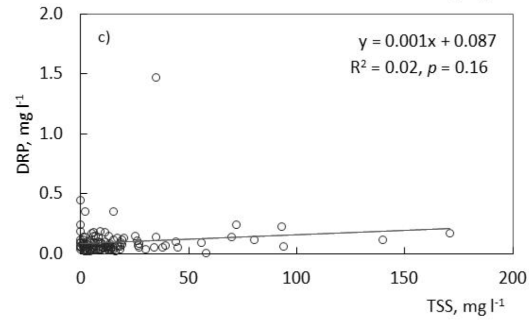
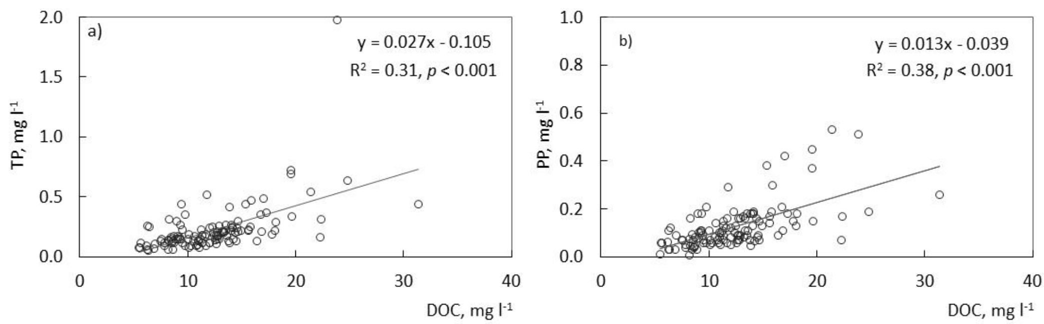


Figure 7a. Relationship between concentrations (mg l^{-1}) of total suspended solids (TSS) and a) total phosphorus (TP), b) particulate phosphorus (PP) and c) dissolved reactive phosphorus (DRP) in individual water samples (n = 117) taken in the small agricultural sub-catchment during 2011−2015 (Paper III). Note difference in scale of Y-axis.



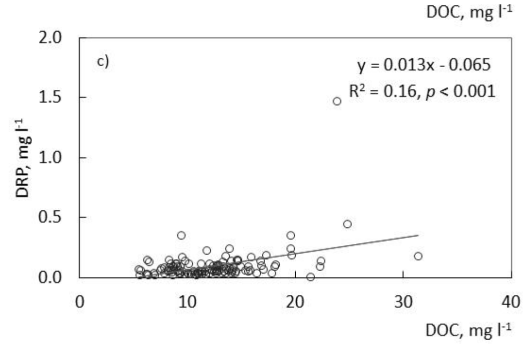


Figure 7b. Relationship between concentrations (mg l^{-1}) of dissolved organic carbon (DOC) and a) total phosphorus (TP), b) particulate phosphorus (PP) and c) dissolved reactive phosphorus (DRP) in individual water samples (n = 117) taken in the small agricultural sub-catchment during 2011−2015 (Paper III). Note difference in scale of Y-axis.

In the small-scale simulated snowmelt experiment on clay soil (this thesis), a strong positive relationship between the concentrations of TSS and TP (R^2 = 0.70) as well as PP (R^2 = 0.80) concentrations when all individual water samples in 2012−2013 were included (Figure 8). The respective coefficient of determination was higher in 2013 than in 2012. However, there was no or a weak linear relationship between TSS and TP or PP on a very fine sandy loam over the years 2011−2013 (Figure 9) or within each year studied (Paper

II). On clay soil in 2013, the TSS losses and the relative increase in TSS losses tended to be greater, with the increasing amount of autumn regrowth, compared with in 2012. This indicates that the nature of TSS might be partly related to organic matter, originating frost injured vegetation. On a very fine sandy loam, a slightly stronger relationship emerged between the concentrations of DOC and P than between the concentrations of TSS and P when all individual water samples were included (Figure 9). Generally, organic P has been found to comprise 33−49% of TP transported in total dissolved and total particulate P fractions from a clayey experimental field under grazed grassland (Haygarth et al. 1998). In this thesis, the results revealed positive relationship between DOC and P concentrations, indicating that DOC and P losses are coupled in grassland dominated areas, as could be anticipated due to vegetation cover, organic residues and slurry inputs. Organic molecules contain P as an important part of their structure and consequently, the increased loss of DOC will likely lead to the increase in the P loss. In addition, soluble organic compounds have been shown to be capable of mobilising P from soil by *e.g.* competition between OM and P for sorption sites (Guppy et al. 2005). Overall, these results suggest that turbidity- or TSS-based estimation of runoff P concentration is probably not appropriate for agricultural catchments containing grasslands and forests, with their relatively high proportion of DRP in TP. A need for P monitoring based on water sampling followed by chemical analysis in the laboratory or *in situ* was evident in the grassland-based sub-catchment studied here.

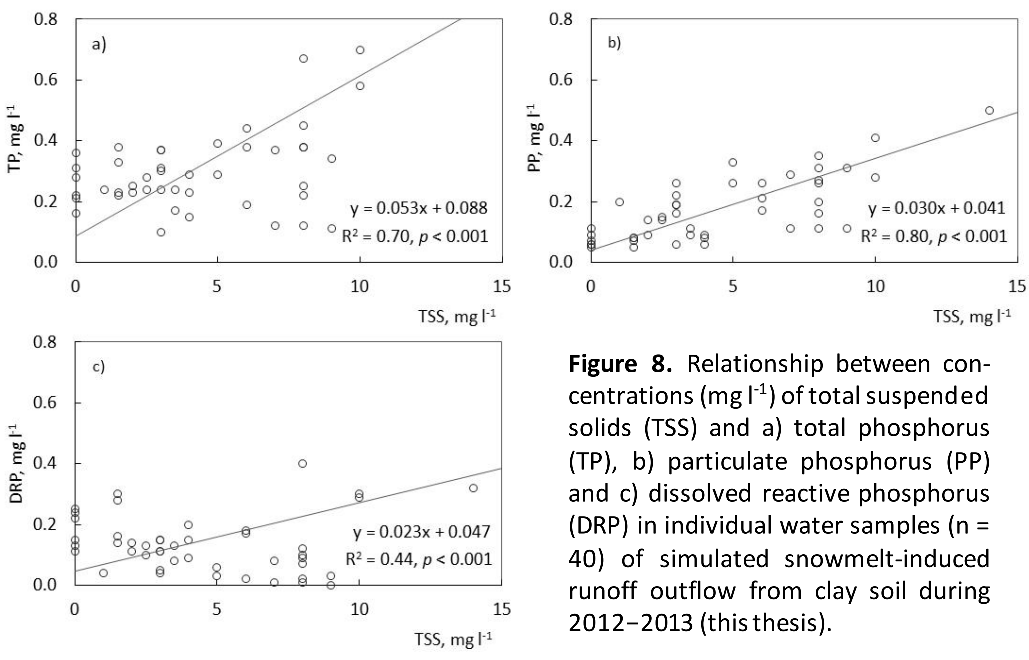
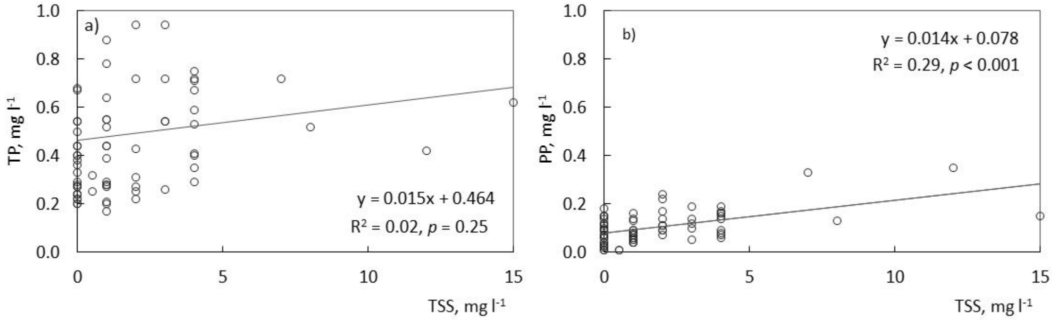


Figure 8. Relationship between concentrations (mg l^{-1}) of total suspended solids (TSS) and a) total phosphorus (TP), b) particulate phosphorus (PP) and c) dissolved reactive phosphorus (DRP) in individual water samples (n = 40) of simulated snowmelt-induced runoff outflow from clay soil during 2012−2013 (this thesis).



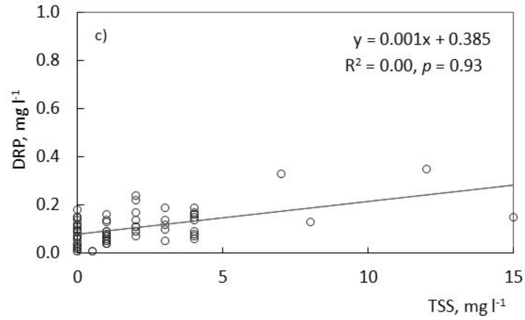
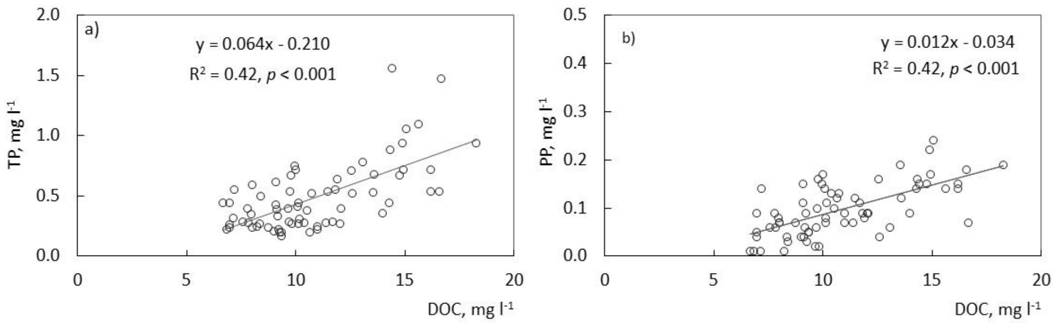


Figure 9a. Relationship between concentrations (mg l^{-1}) of total suspended solids (TSS) and a) total phosphorus (TP), b) particulate phosphorus (PP) and c) dissolved reactive phosphorus (DRP) in individual water samples (n = 71) of simulated snowmelt-induced runoff outflow from very fine sandy loam soil during 2011−2013 (Paper II).



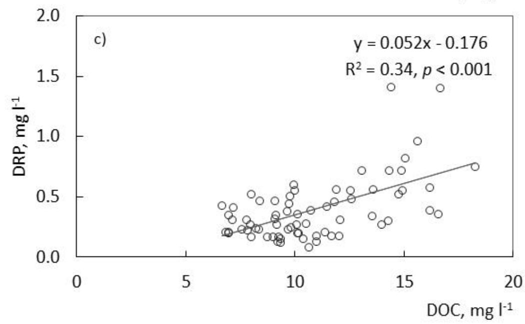


Figure 9b. Relationship between concentrations (mg l^{-1}) of dissolved organic carbon (DOC) and a) total phosphorus (TP), b) particulate phosphorus (PP) and c) dissolved reactive phosphorus (DRP) in individual water samples (n = 69) of simulated snowmelt-induced runoff outflow from very fine sandy loam soil during 2011−2013 (Paper II). Note difference in scale of Y-axis.

3.4. Phosphorus losses in short-term ley rotation

The mean annual TP load from the agricultural sub-catchment during the five-year monitoring period was 1.0 kg ha^{-1} (range 0.6−1.5 kg ha^{-1}), the respective value being 0.8 kg ha^{-1} (0.3−1.1 kg ha^{-1}) for the whole catchment (Paper III). This corresponded well with the mean annual specific TP loss of 1.1 kg ha^{-1} reported by Vuorenmaa et al. (2002) and Tattari et al. (2017) for agricultural land in small agricultural catchments during 1981−2010. For the same small catchments during 1981−2010, Tattari et al. (2017) found a mean annual specific loss of on average 15.5 kg ha^{-1} yr^{-1} for TN, which is lower than the mean annual TN loss of 19 kg ha^{-1} estimated for the agricultural sub-catchment (range 13−30 kg ha^{-1}) (Paper III).

Annual variations in erosion rate and PP losses within different cultivation treatments have been shown to be substantially larger for autumn tillage treatments than for direct sowing and grass ley treatments, whereas the opposite is true for DRP losses (Puustinen et al. 2005). The difference in erosion and PP losses between the different hydrological conditions prevailing during autumn-winter is also smaller in treatments with permanent vegetation cover than in unvegetated treatments. In the case of DRP, P losses tend to be relatively insensitive to weather-driven hydrological conditions (Puustinen et al. 2007). However, there was substantial seasonal variation in TP and DRP losses, and in TSS losses, from the agricultural sub-catchment characterised by grassland in Paper III. In addition, the average proportion of TP load transported as DRP (mean 44%, range 32−56%) was higher than that reported for well-monitored Finnish agricultural catchments under cereal cultivation (Pengerud et al. 2015, Tattari et al. 2017), reflecting relatively high algae-available P losses typical for grasslands. Generally, DRP constituted a lower proportion of TP losses at the small catchment scale, being 34% (range 28−38%) for the whole catchment (Paper III), than in the small-scale simulated snowmelt experiments (Paper II, this thesis). This can be attributed to the different spatial scales of the studies (Haygarth et al. 2012), and the combined influence of variations in hydrological conditions, land use and management practices.

Excluding the autumn of 2014, the spring season had the largest proportion of discharge in the agricultural sub-catchment during the five-year monitoring period (Figure 10) and consequently most of the TN load was mainly delivered during the spring snowmelt period (Paper III). Spring snowmelt has been reported to control TP load in surface runoff from plots in the study region (Järvenranta et al. 2014). In this thesis, however, spring season made up the largest proportion of TP to annual load only in two out of five monitored years in the agricultural sub-catchment (Paper III). The highest monthly TP load during the monitoring period, with a high proportion of DRP to TP, was produced in combination with high sample P concentration and rainfall-induced high discharge in November 2014 (Paper III). This high autumn TP flux was probably attributable to flushing out of P reserves that had been mineralised and accumulated during the summer (Haygarth et al. 2012), and to the effects of freezing phenomena on P release as discussed above. With recent changes in the seasonality of flow water volume, Räike et al. (2020) reported a decrease in TP export during spring snowmelt period and an increase in TP export during winter months in Finnish river basins during the past two decades. These results also demonstrate the importance of wet summer and autumn periods for P loading from grasslands in east-central Finland.

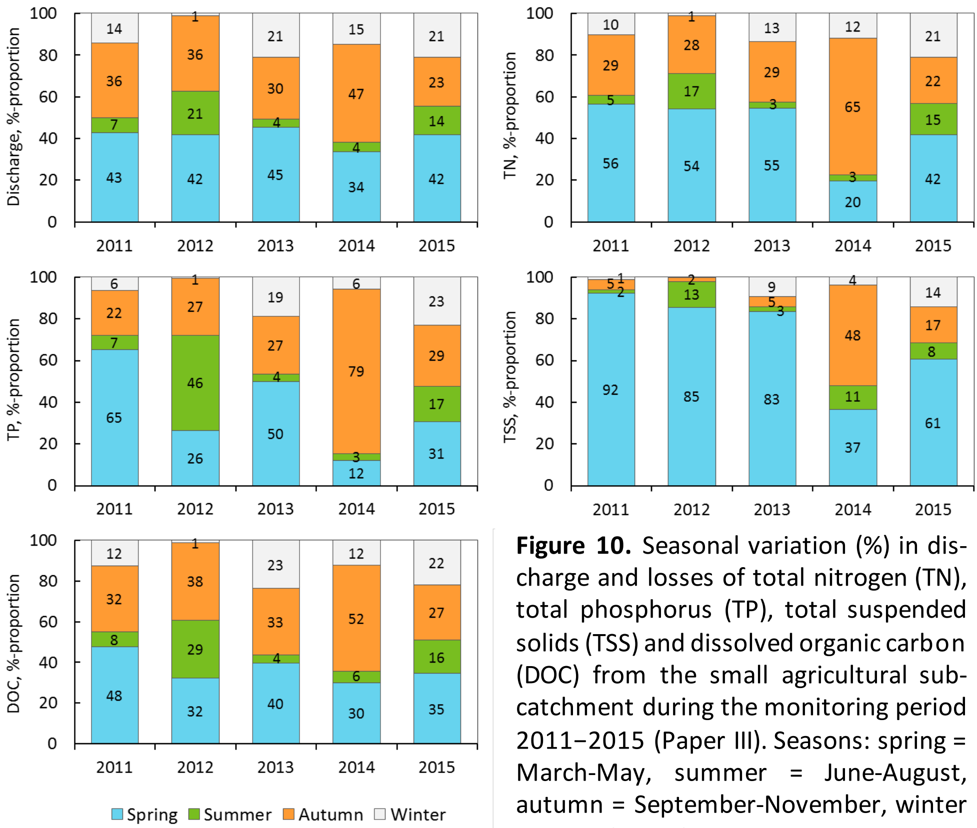


Figure 10. Seasonal variation (%) in discharge and losses of total nitrogen (TN), total phosphorus (TP), total suspended solids (TSS) and dissolved organic carbon (DOC) from the small agricultural sub-catchment during the monitoring period 2011−2015 (Paper III). Seasons: spring = March-May, summer = June-August, autumn = September-November, winter = December-February.

The results in Paper III showed that the P losses from the agricultural sub-catchment, which is representative of grassland-based dairy farming areas in east-central Finland, were comparable to the P losses from agricultural land under cereal cultivation. In Finnish short-term ley farming, the topsoil is mixed by ploughing during grass ley renewal, which also reduces the vertical P stratification developing from P fertiliser application and OM accumulation to the soil surface. In general, the recent decreasing trend in soil P status has probably lowered the P loading potential from intensely managed grasslands. However, due to climate change, precipitation is projected to increase in spring, autumn and especially winter (Ruosteenoja et al. 2011), enhancing the risk of increased nutrient losses from cultivated fields to surface waters in northern Europe (IPCC 2007). Large-scale changes to agriculture are needed to limit the projected increase in winter P loads (Ockenden et al. 2017). Although grasslands are less prone to erosion, they are susceptible to eutrophication-relevant losses of algae-available DRP, which are difficult to control. Consequently, efficient management practices are needed to compensate for anticipated climate-related increases in nutrient loading.

3.5. Assessment of water sampling strategy

In the monitoring areas in the small agricultural and forested catchment (Paper III), composite (automatic) water sampling covered a very representative range of high flows during the snowmelt period. In contrast, high-flow events induced by intense rainfall during summer and autumn were not systematically captured by the coarser grab sampling frequency, resulting in uncertainties in flux estimates during these periods. Based on high-frequency *in situ* turbidity measurements, Lannergård et al. (2019) showed that TP fluxes calculated from grab samples by the linear interpolation method resulted in under- and overestimation (-10% to +13%), but corresponded well with annual fluxes in five of six years in a Swedish catchment (28% fields). Their findings highlighted the influence of high stream discharge at the time of sampling on the flux magnitude and the dependence of the accuracy of high-frequency measurements on temporal scale and the characteristics of the catchment in question. Based on national-scale river water quality monitoring programmes in Norway, Sweden and Denmark, Cassidy et al. (2018) evaluated flow-weighted composite sampling approaches (n = 26–52 samples per year) for TP with respect to *e.g*. spatial coverage, temporal resolution and cost. They found that a dynamic fortnightly sampling approach based on estimated river discharge using two-week forecast rainfall appeared to be most reliable. Assessment of temporal variability in nutrient flux dynamics associated with rapid hydrological changes, including short-term high discharge episodes induced by intense rainfall events, requires higher water sampling frequency or high-frequency *in situ* monitoring, as suggested by *e.g.* Valkama (2018), Lannergård et al. (2019), Lloyd et al. (2019) and Villa et al. (2019). In this thesis, water sampling was targeted at the high flow period in the springtime, starting before the spring flood, but also succeeded in capturing part of the flow peaks during heavy rainfall in summer and autumn. The sampling frequency can be considered adequate for providing a close approximation of average annual concentrations and fluxes of P, N, DOC and TSS. However, there were large seasonal variations in the hydrological conditions and amount of P, N, DOC and TSS losses during the study period, suggesting that higher water sampling frequency should be also targeted at the wet growing season and autumn periods in future.

4. Summary and conclusion

After the last harvest of fertilised grass leys or unfertilised perennial grasses in buffer zones, the grass continues to grow, taking up nutrients from the soil. In grasslands, however, some of the nutrients incorporated into aboveground biomass of autumn regrowth may also be released into the environment. The conclusion of this study was that grasslands can release substantial amounts of plant-derived P due to freezing and thawing after the growing season. At the fertilised grass ley sites examined in this thesis, aboveground biomass amounted to 2400 kg DM ha^{-1} with a TP content of 4.6 kg ha^{-1} in October-November. It averaged almost 3800 kg DM ha^{-1}, with a TP content of 6.0 kg ha^{-1}, at grass ley sites where the second cut was not harvested. At unfertilised grass buffer zone sites, the greatest TP reduction (0.5−6.1 kg ha^{-1}) in the stand occurred between samplings in October and November, *i.e.* before and after the first frost occurrences. The natural freezing and thawing to which biomass was subjected to prior to the sampling in November resulted in enhanced P solubility. Part of the TP reduction was probably attributable to remobilisation of nutrients from shoot to roots due to winter acclimation of perennials, and part to adsorption of released P to soil. Overall, the results showed that grassland vegetation can be a source of P release to surface runoff water in boreal conditions.

In the simulated snowmelt experiments, even up to almost 0.70 kg TP ha^{-1} was released from fertilised silage grass leys on clay and very fine sandy loam soils with satisfactory soil P status (6.2−10.3 mg P_{Ac} l^{-1}). In addition, a high proportion of DRP, averaging 44−77% of TP concentration, was observed in surface runoff outflow. Higher TP concentrations and losses in runoff outflow were observed in different treatments on grass sods lifted in 2013 than in 2012. The elevated P losses in 2013 were attributed to a low degree of soil insulation as a consequence of exceptionally thin snow cover in winter 2013 when the lifted grass sods were stored outside in prevailing winter conditions until simulated snowmelt. These results indicate that reduced or lack of permanent snow cover may enhance the risk of freezing damage to vegetation and consequently, increase the risk of P losses. While the advantage of plant P removal with harvested ley biomass was connected with weather conditions, harvesting of grass sites used as buffer zones along streams and ditches is recommended due to the potential of these zones to act as a substantial source of plant-derived P losses to the neighbouring watercourse.

A protective cover of aboveground biomass, together with an upper layer of belowground biomass, efficiently prevented soil erosion and resulted in low soil erosion rates from grasslands. In small-scale simulated snowmelt experiments, the mean erosion rate measured as TSS varied from 0.2 to 11 kg ha^{-1}, associated with an average total runoff outflow volume of 76 mm, representing dense-growing fertilised grass leys. The results from the small-scale approaches were complemented with five-year monitoring data for a small 3.2 km^2 agricultural and forested catchment comprising grassland, cereals and forest areas and representing a typical agricultural area in east-central Finland. In the agricultural sub-catchment, with 93% fields characterised by flat topography and coarse-textured soils, grasslands constituted at least half the cultivated area and the annual erosion rate varied from 46 to 287 kg ha^{-1} over the five-year monitoring period. This wide variation in erosion rate was partly attributable to different hydrological conditions and partly to the grass-cereal rotation practised in the catchment, in which agricultural land was under grassland and cereals. The results also indicated that a substantial part of P losses may have been associated with losses of organic material. Only weak linear relationships were found between concentrations of TSS and TP or PP, indicating that using turbidity values for indirect estimation of runoff TP or PP is probably not appropriate in typical agricultural catchments in east-central Finland. Consequently, there is a need for P monitoring based on water samples, followed by chemical analysis in the laboratory or *in situ.*

Mean annual TP load from the agricultural sub-catchment was 1.0 kg ha^{-1} (range 0.6−1.5 kg ha^{-1}) and corresponded well with mean annual specific TP losses reported for agricultural land under cereal cultivation within intensively monitored Finnish agricultural catchments. However, a relatively high proportion of the TP load from the agricultural sub-catchment was transported in the form of DRP (mean 44%), which is readily available to the algae. The susceptibility of grassland to such P losses is problematic, as they are difficult to control. In conventional Finnish grass ley cultivation, part of the grassland area is typically renewed after autumn ploughing. The associated changes in hydrological conditions, land use, management practices as well as potential changes in soil P status result in relatively high year-to-year variability in P losses. Consequently, nutrient losses and erosion rates from short-term ley grasslands should be considered for the whole ley rotation, including the ley establishment and renewal year.

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